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(71) Applicant: SRI INTERNATIONAL [US/US]; 333 Ravenswood Avenue, Menlo Park, CA 94025-3493 (US).

(72) Inventors: NARANG, Subhash, C.; 728 Garland Drive, Palo Alto, CA 94303 (US). VENTURA, Susanna, C.; 424 Becker Lane, Los Altos, CA 94022 (US). ZHAO, Ming; 1010 Noel Drive #32, Menlo Park, CA 94025 (US). SMEDLEY, Stuart; 298 E. O'Keefe Street, Menlo Park, CA 94025 (US). KOOLPE, Gary; 2350 Laura Lane, Mountain View, CA 94043 (US). DOUGHERTY, Brian, J.; 1309 Mills Street #C, Menlo Park, CA 94025 (US).

(74) Agent: FISH, Robert, D.; Suite 706, 1440 N. Harbor Boulevard, Fullerton, CA 92835 (US).

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(54) Title: NONFLAMMABLE/SELF-EXTINGUISHING ELECTROLYTES FOR BATTERIES

(57) Abstract

Novel fire-retardant electrolyte compositions are provided. These compositions comprise a lithium salt dissolved in a fire-retardant solvent selected from the group consisting of phosphates, phospholanes, cyclophosphazenes, silanes, fluorinated carbonates, fluorinated polyethers and mixtures thereof. The electrolyte composition optionally contains a CO_2-generating compound. Also provided are fire-retardant batteries and fire-retardant conductive films formulated with such compositions, as well as methods of manufacturing such films.

5   NONFLAMMABLE/SELF-EXTINGUISHING
                       ELECTROLYTES FOR BATTERIES

Reference to Government Grant
             This invention was made with Government
10   support.   The Government has certain rights in the
     invention.

Technical Field
             The present invention relates generally to
15   batteries.   More particularly, the invention relates to a
     fire-retardant electrolyte composition and batteries
     fabricated to contain the composition.   Also within the
     scope of the present invention are conductive films
     comprising the fire-retardant electrolyte composition.
20

Background of the Invention
             Recently, solid-state, high energy-density
     batteries have been developed that use metallic lithium
     as the anode.   Lithium metal is a preferred anode
25   material for batteries because its thermodynamic and
     kinetic qualities are superior to those of other
     materials.   Lithium is a good conductor of electricity
     and heat and has an electrochemical equivalence of 3.86
     Ah g^{-1} and a standard electrode potential of -3.5 V.   In
30   addition, lithium is soft and malleable, can be readily
     extruded into thin sheets.   However, it is well known
     that lithium is reactive with water and other reagents
     (see, e.g., Linden, D., Ed., Handbook of Batteries and
     Fuel Cells, McGraw-Hill, NY, 1984).
35

Typically, the liquid electrolyte solvent used
in lithium batteries is a dipolar aprotic solvent.
Aprotic solvents are used due to the absence of labile
hydrogen atoms that would react with lithium to evolve
5   hydrogen. Dipolar solvents, i.e., those having a strong
dipole moment in the molecule, are used because they have
substantial solvation energies for the electrolyte salt
which results in better salt dissolution of the salt, and
because they have a higher dielectric constant for the
10   solvent, i.e., better ionic dissociation.

Solvents such as propylene carbonate ("PC"),
ethylene carbonate ("EC"), diethyl carbonate ("DEC"),
1,2-dimethoxyethane, and methylformate have been used in
lithium batteries either in pure form or in solvent
15   mixtures. These solvents provide high conductivities in
the presence of suitable lithium salts. However, the
chemical stability and safety of these solvents has
recently been questioned (see, e.g., Bowden et al. (1992)
"Rechargeable Lithium Batteries, A Survey of the
20   Published Literature, in Proc. Fourth Int'l Rechargeable
Battery Seminar). Improved liquid organic electrolytes
with higher conductivities than these solvents are needed
to meet the power requirements for many consumer
applications, especially at low temperatures.

25   In addition, commercially available lithium
cells, with a pure lithium anode, are presently available
only as primary cells and are not recommended for use as
secondary cells. This limitation is due to the
reactivity of the electrolyte system with the lithium
30   metal.

There are at least two disadvantageous effects
that arise from the reaction of lithium with the
electrolyte in a lithium cell: the exothermic liberation
of heat, and the formation of a passivating film on the
35   anode surface. Liberation of heat is a problem because

under some circumstances it could lead to an explosive
release of energy and reactive materials, thereby
creating a hazard for both the operator and the device
that is being powered by the cell. Highly exothermic

5   reactions have been known to occur when primary lithium
batteries are subjected to temperatures above the
recommended levels or when some rechargeable cells are
subjected to unusual or severe conditions of recharging
(see, e.g., Ebner et al. (1982) in *Proc. 30th Power*

10   *Sources Symp.*, p 119). Primary lithium cells using, for
example, a lithium thionylchloride system, have been
known to undergo high exothermic reactions when subjected
to temperatures above or below the recommended
temperatures. In the case of secondary cells, subjecting

15   the cells to unusual or severe recharging conditions and
deposition of lithium in a highly porous film on the
anode have led to similar disastrous results.
Pasquariello et al. (1993) *Proc. Symp. Lithium Batteries*
93-24:106.

20   In addition to the intrinsic reactivity of
lithium toward the electrolyte, the lithium in
rechargeable cells will deposit to form a dendritic
layer, which enhances the reactivity of lithium
(Pasquariello et al., *supra*).

25   The formation of passive films on lithium has
been shown to be one reason for the loss of capacity of
lithium cells on repeated cycling (Shen et al. (1984)
*Capacity Decline Studies of Rechargeable Lithium
Batteries*, McGraw-Hill, NY). The film can isolate the

30   anode from the electrolyte, thereby providing a high
impedance path and a degradation in cell performance. In
addition, lithium metal tends to "deposit out" on the
surface of the film rather than on the lithium anode; the
deposited lithium is electrically isolated from the anode

35   and is unavailable for later discharges.

The problem of lithium reactivity toward the electrolyte has been addressed in various ways. One approach is to use a carbon intercalation compound such as LiC_6 or LiC_{12} with either a liquid or polymeric

5   electrolyte. One disadvantage of this approach is the loss of capacity density (0.37 Ah g^{-1} compared to 3.86 Ah g^{-1} for lithium) and voltage (3.4 v compared to 3.5 V for lithium).

Nevertheless, commercial cells are available

10   that have adopted this approach. Early versions of such a cell had a LiC_{12} anode, a $LiCoO_2$ cathode, and used EC:DEC (in a 1:1 mixture), with lithium hexafluoro-phosphate ($LiPF_6$) salt as the electrolyte. This cell has demonstrated 1200 cycles to 100% depth of discharge,

15   while retaining 77% of its capacity. Megahead (1994) *J. Power Sources* 51:79. Energy densities of about 90-110 Wh kg^{-1} (210-260 Wh dm^{-3}), depending on the cell configuration, have been achieved by this cell. Megahead, *supra*. More recently, versions of this cell

20   manufactured with LiC_6 instead of LiC_{12} as the anode have achieved comparable cycling performance with improved energy density. Although the performance of this cell is adequate, the improvement in energy density that could be obtained by using Li as the anode is significant provided

25   the rechargeability of the Li is improved.

Replacement of lithium with LiC_6 increases the onset temperature of exothermic behavior to 120° C from 100° C for a Li|MnO_2 cell after 25 cycles as measured by accelerated rate calorimetry. Von Slacken et al. (1994)

30   *Proc. Seventh Int'l Meeting on Lithium Batteries*, p. 12. In addition, the heat capacity of the reaction was lower ($1.7-2.0$ cal °K^{-1} versus 2.8 cal °K^{-1} for Li|MnO_2). However, the lithium anode becomes more strongly exothermic as it is cycled (Von Slacken et al., *supra*),

35

presumably because of the formation of a more porous electrode structure and, hence, greater surface area.

A second approach to reduce the problem of lithium reactivity toward the electrolyte is to replace the electrolyte with a polymeric material. This approach would reduce the rate of reaction by imposing a transport limitation on the reaction. However, the conductivity of polymer electrolytes is at least an order of magnitude lower than that of liquid electrolytes, resulting in batteries of lower specific energy and power. Furthermore, this approach requires the use of alternate battery fabrication techniques.

Accordingly, there remains a need to provide safe primary and secondary lithium batteries. Such batteries require an electrolyte that is chemically stable with respect to lithium, is substantially nonflammable, and is compatible with existing electrode and battery fabrication technology. The present invention provides such batteries. The novel batteries do not exhibit the drawbacks exhibited by prior batteries such as combustion under conditions of overcharging, accidental rupture, accidental short-circuiting, and the like.

Summary of the Invention

Accordingly, it is a primary object of the invention to address the aforementioned need in the art by providing a lithium battery containing a fire-retardant electrolyte composition.

It is another object of the invention to provide such a battery comprising an anode, a cathode and a fire-retardant electrolyte composition.

It is still another object of the invention to provide such a battery in which the electrolyte composition comprises a lithium salt dissolved in a

-6-

solvent selected from the group consisting of a phosphate, a pholane, a cyclophosphazene, a silane, a fluorinated carbonate, a fluorinated polyether, and mixtures thereof.

5   It is still another object of the invention to provide a battery comprising a fire-retardant electrolyte composition as above, wherein the composition further includes a CO_2-generating compound.

          It is yet another object of the invention to
10   provide a fire-retardant electrolyte composition comprising a lithium salt dissolved in a solvent selected from the group consisting of a phosphate, a phospholane, a cyclophosphazene, a silane, a fluorinated carbonate, a fluorinated polyether, or mixtures thereof, as described
15   above, and wherein the fire-retardant electrolyte composition optionally includes a film-forming polymeric material.

          It is a further object of the invention to provide a fire-retardant electrolyte composition as
20   described above and, optionally, containing a CO_2-generating compound.

          It is still a further object of the invention to provide a fire-retardant conductive film generally formed from a combination of a lithium salt or a single-
25   ion conducting polymer electrolyte dissolved in a fire-retardant electrolyte solvent as described above, an amount of a film-forming polymeric material such as poly(vinylidene fluoride) effective to enhance the mechanical strength of the resulting electrolyte
30   composition, and, optionally, a CO_2-generating compound. In this manner, thin but nevertheless highly conducting films may be formulated having fire-retardant physical properties.

          Additional objects, advantages and novel
35   features of the invention will be set forth in part in

the description that follows, and in part will become
apparent to those skilled in the art upon examination of
the following, or may be learned by practice of the
invention.

5   In a primary aspect of the invention, batteries
are provided that comprise an anode, a cathode and a
fire-retardant electrolyte composition including a
lithium salt dissolved in a solvent, wherein the solvent
is a phosphate having the structure as shown in Formula
10   (I)

$$
\begin{array}{c}
OR^1 \\
| \\
(I) \qquad O=P-OR^2 \\
| \\
OR^3
\end{array}
$$

15

wherein R^1, R^2 and R^3 are independently selected from the
group consisting of (a) C_1-C_6 alkyl terminally
substituted with 0 to 3 halogen atoms and containing 0 to
3 ether linkages, (b) $Si(R^4)_3$ and (c) $B(OR^4)_2$, wherein
20   the R^4s are independently C_1-C_6 alkyl containing 0 to 3
ether linkages or C_1-C_3 alkoxy, and optionally wherein
two or more compounds of structure (I) are linked
together by an ether linkage, a pholane having the
structure as shown in Formula (II),

25

$$
(II) \qquad
\begin{array}{c}
\left[\begin{array}{c} O \\ \diagdown \\ O \diagup \end{array} P \diagdown \begin{array}{c} R^5 \\ \diagdown \\ OR^6 \end{array} \right.
\end{array}
$$

wherein R^5 is selected from the group consisting of oxy
30   or a pair of electrons and, when R^5 is a pair of
electrons, R^6 is C_1-C_6 alkyl terminally substituted with
0 to 3 halogen atoms and containing 0 to 3 ether

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linkages, a cyclophosphazene having the structure as
shown in Formula (III),

$$
\text{(III)} \qquad \left[\begin{array}{c} R^7 \\ | \\ N{=}P \\ | \\ R^8 \end{array} \right]_n
$$

5

wherein n is an integer from 3 to 6 and R^7 and R^8 are
independently selected from the group consisting of
hydrogen, halogen and $-OR^9$ wherein R^9 is C_1-C_6 alkyl
terminally substituted with 0 to 3 halogen atoms and
containing 0 to 3 ether linkages, with the proviso that
when one of R^7 or R^8 is $-OR^9$, the other is halogen, a
silane having the structure as shown in Formula (IV),

10

15

$$
\text{(IV)} \qquad \begin{array}{c} R^{10} \\ | \\ R^{11}{-}Si{-}R^{12} \\ | \\ R^{13} \end{array}
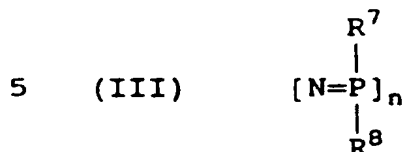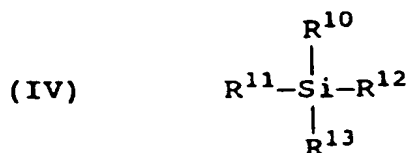$$

20

wherein R^{10}, R^{11}, R^{12} and R^{13} are independently selected
from the group consisting of (a) C_1-C_6 alkyl terminally
substituted with 0 to 3 halogen atoms and containing 0 to
3 ether linkages and (b) $-OR^{14}$ wherein R^{14} is C_1-C_6 alkyl
terminally substituted with 0 to 3 halogen atoms and
containing 0 to 3 ether linkages, and optionally wherein
two or more compounds of structure (IV) are linked
together by a siloxane linkage, a fluorinated carbonate
having the structure as shown in Formula (V),

25

30

$$
\text{(V)} \qquad R^{15}{-}O{-}\overset{\overset{\textstyle O}{\|}}{C}{-}O{-}R^{16}
$$

wherein R^{15} and R^{16} are independently selected from the
group consisting of (a) perfluorinated or partially

35

fluorinated C_1-C_{10} alkyl containing 0 to 3 ether linkages and (b) -OR^{17} wherein R^{17} is perfluorinated or partially fluorinated C_1-C_{10} alkyl containing 0 to 3 ether linkages or wherein R^{15} and R^{16} are linked together to form a perfluorinated or partially fluorinated C_1-C_{10} alkyl bridge, a fluorinated polyether having the structure shown in Formula (VI)
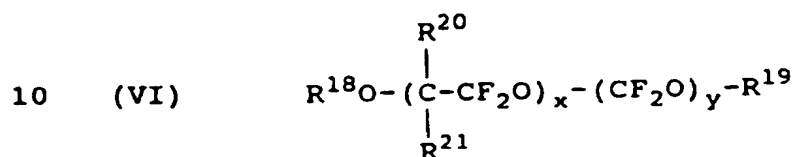
$$\text{(VI)} \qquad R^{18}O-\underset{\underset{R^{21}}{|}}{\overset{\overset{R^{20}}{|}}{C}}-CF_2O)_x-(CF_2O)_y-R^{19}$$

wherein R^{18} and R^{19} are independently perfluorinated or partially fluorinated C_1-C_{10} alkyl, R^{20} and R^{21} are independently selected from the group consisting of -F and perfluorinated or partially fluorinated C_1-C_{10} alkyl, and x and y are independently selected such that the polymer has a number average molecular weight in the range of about 400 to about 10,000, or mixtures of such phosphates, phospholanes, cyclophosphazenes, silanes, fluorinated carbonates, and fluorinated polyethers, and wherein the fire-retardant electrolyte composition optionally includes a film-forming polymeric material.

In further aspects of the invention, fire-retardant electrolyte compositions and fire-retardant conductive films comprising the solvents as described above are provided. The fire-retardant electrolyte compositions and conductive films disclosed and claimed herein may be used in batteries, for example, a solid state Li_xC_6/electrolyte/$LiCoO_2$, Li/electrolyte/TiS_2, or Li/electrolyte/V_6O_{13} battery, or in electrochemical devices such as fuel cells, supercapacitors, electrochromic devices and sensors, or the like.

Brief Description of the Figures

        FIG. 1 shows the potential profile for the battery described in Example 6 upon cycling.

        FIG. 2 shows the exothermic behavior for
5   strips of lithium metal immersed in the triethylphosphate (47.5% v/v):methoxyethyl diethyl phosphate (47.5% v/v):di-*tert*-butyl dicarbonate (5% v/v) mixture (solid line) and for the electrolyte used in a commercial primary lithium battery (dashed line) as described in
10   Example 8.

Detailed Description of the Invention

        The practice of the present invention will employ, unless otherwise indicated, conventional
15   techniques of synthetic chemistry, electrochemistry, and polymer chemistry that are within the skill of the art. Such techniques are explained fully in the literature. *See*, e.g., Kirk-Othmer's Encyclopedia of Chemical Technology, in House's Modern Synthetic Reactions, in
20   C.S. Marvel and G. S. Hiers' text *ORGANIC SYNTHESIS*, Collective Volume 1, or the like.

        All patents, patent applications and publications cited herein, whether *supra* or *infra*, are hereby incorporated by reference in their entirety.
25   Definitions:

        Before describing the present invention in detail, it is to be understood that this invention is not limited to particular salts, methods of synthesis, solvents, or the like, as such may vary. It is also to
30   be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

        It must be noted that, as used in this specification and the appended claims, the singular forms
35   "a," "an" and "the" include plural referents unless the

content clearly dictates otherwise. Thus, for example, reference to "a fire-retardant electrolyte composition" includes mixtures of such composition, reference to "a solvent" includes more than one such solvent, reference

5   to "a CO_2 generator" includes mixtures of CO_2 generators, and the like.

In this specification and in the claims which follow, reference will be made to a number of terms which shall be defined to have the following meanings:

10   The terms "fire-retardant" and "nonflammable" are used interchangeably herein to indicate a reduction or elimination of the tendency of a combustible material to burn, i.e., a "fire-retardant" material is one having a lower ignition susceptibility or, once ignited, lower

15   flammability. Thus, a fire-retardant electrolyte composition is one in which the basic flammability has been reduced as measured by accelerated rate calorimetry (see, e.g., Von Slacken et al., supra), or by one of the art-accepted standard flame or heat impingement tests, or

20   other standard test of reduced flammability, for example, ASTM D2863 (limiting oxygen index) (see, e.g., Tests for Flammability of Plastic Materials for Parts in Devices and Appliances, Underwriters Laboratories, Northbrook, IL, 1991; National Fire Codes, National Fire Protection

25   Assoc., Quincy, MA, 1992; Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products, American Society for Testing and Material, Philadelphia, Pa., 1991; see, also, "Fire Retardants" in Encyclopedia of Polymer Science and Engineering, Vol. 10,

30   page 930-1022, 2nd ed., John Wiley and Sons, NY, 1988).

The terms "CO_2-generating compound" and "CO_2 generator" are used interchangeably to refer to a chemical source of carbon dioxide. A CO_2 generator typically yields CO_2 upon decomposition. CO_2 generators

35   that are preferred for use in the claimed electrolyte

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compositions are those that do not produce decomposition
byproducts that are incompatible, either chemically or
electrochemically with the electrolyte or other battery
materials. Test cells containing such CO_2 generators in
5 addition to flame-retardant electrolytes have improved
discharge-recharge cycling properties in a manner
consistent with the report by Aurbach et al. (1994) *J.
Electrochem. Soc.* <u>141</u>:603.

The term "alkyl" as used herein refers to a
10 branched or unbranched saturated hydrocarbon group of 1
to 24 carbon atoms, such as methyl, ethyl, n-propyl,
isopropyl, n-butyl, isobutyl, t-butyl, octyl, decyl,
tetradecyl, hexadecyl, eicosyl, tetracosyl and the like.
Preferred alkyl groups herein contain 1 to 12 carbon
15 atoms. The term "lower alkyl" intends an alkyl group of
one to six carbon atoms.

The term "alkenyl" refers to a branched or
unbranched hydrocarbon chain containing from 2 to 24
carbon atoms and at least one double bond. "Lower
20 alkenyl" refers to an alkenyl group of 2 to 6, more
preferably 2 to 5, carbon atoms. The term "fluorinated
lower alkenyl" intends an alkenyl group of one to six
carbon atoms in which at least one hydrogen atom, and
optionally all hydrogen atoms, are replaced with fluorine
25 atoms.

The term "alkoxy" as used herein intends an
alkyl group bound through a single, terminal ether
linkage; that is, an "alkoxy" group may be defined as -OR
wherein R is alkyl as defined above. A "lower alkoxy"
30 group intends an alkoxy group containing one to six, more
preferably one to four, carbon atoms.

The term "aryl" as used herein refers to a
monocyclic aromatic species of 5 to 7 carbon atoms, and
is typically phenyl. Optionally, these groups are
35 substituted with one to four, more preferably one to two,

lower alkyl, lower alkoxy, hydroxy, and/or nitro
substituents.

The term "aralkylene" is used to refer to
moieties containing both alkylene and monocyclic aryl
species, typically containing less than about 12 carbon
atoms in the alkylene portion, and wherein the aryl
substituent is bonded to the structure of interest
through an alkylene linking group. Exemplary aralkylene
groups have the structure $-(CH_2)_j-Ar$ wherein j is an
integer in the range of 1 to 6.

"Halo" or "halogen" refers to fluoro, chloro,
bromo or iodo, and usually relates to halo substitution
for a hydrogen atom in an organic compound. "Haloalkyl"
refers to an alkyl moiety in which one or more of the
hydrogen atoms is substituted by a halo atom. Of the
halos, fluoro is generally preferred. The term "lower
haloalkyl" intends an alkyl group of one to six carbon
atoms in which at least one hydrogen atom, and
optionally, all hydrogen atoms, are replaced with halogen
atoms. The term "perhalogenated" refers to a compound in
which all of the hydrogen atoms have been replaced by
fluorine atoms, while the phrase "partially halogenated"
refers to a compound in which less than all of the
hydrogen atoms have been replaced by fluorine. Thus, a
perfluorinated alkyl is a branched or unbranched
saturated hydrocarbon group as defined above in which all
of the hydrogen atoms have been replaced by fluorine
atoms.

"Optional" or "optionally" means that the
subsequently described circumstance may or may not occur,
and that the description includes instances in which said
circumstance occurs and instances in which it does not.
For example, the phrase "optionally including a film-
forming polymeric material" means that a film-forming
polymeric material may or may not be present and that the

description includes both the instance when the film-
forming polymeric is present and the instance when the
film-forming polymeric material is not present.

5   In one embodiment of the invention, there is
provided a battery comprising an anode, a cathode and a
fire-retardant electrolyte composition comprising a
lithium salt dissolved in a solvent that includes low-
flammability, self-extinguishing, i.e., fire-retardant,
solvents that are chemically stable to lithium. Such
10   fire-retardant solvents include phosphates, phospholanes,
cyclophosphazenes, silanes and mixtures of such solvents.

          Many fire-retardant solvents that are useful in
the invention disclosed and claimed herein are
commercially available or can be readily synthesized
15   using conventional techniques well known to those skilled
in the art of synthetic organic chemistry or which may be
found in relevant texts.

          Fire-retardant phosphate solvents that are
useful in the invention include those having the
20   structure as shown in Formula (I)

$$(I) \qquad \begin{array}{c} OR^1 \\ | \\ O{=}P{-}OR^2 \\ | \\ OR^3 \end{array}$$

25

wherein R^1, R^2 and R^3 are as defined above and optionally
wherein two or more compounds of structure (I) are linked
together by an ether linkage. Commercially available
phosphate solvents include, for example, trimethyl-
30   phosphate (Aldrich) and triethylphosphate (Aldrich).
Alternatively, triethylphosphate, a well-known flame
retardant and plasticizer (see, e.g., U.S. Patent No.
3,909,484 to Beavon; Nametz (1967) Ind. Eng. Chem. 59:99;
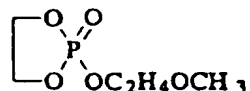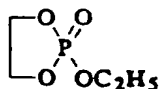and Larsen et al. (1979) J. Fire Retardant Chem. 6:182)
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-15-

can be readily manufactured from diethyl ether and
phosphorus pentoxide via a metaphosphate intermediate as
described in U.S. Patent Nos. 2,430,569 and 2.407,279 to
Hull et al. Other such phosphates can be synthesized
5   using conventional synthetic techniques. Thus, tris-
(methoxyethyl)phosphate, tris-(methoxyethoxy-
ethyl)phosphate and tris-(1,1',1"-trifluoroethyl)-
phosphate can be prepared by reaction of phosphoryl-
chloride with 2-methoxyethanol, 2-(2-methoxy)ethoxy-
10   ethanol and 1,1',1"-trifluoroethanol, respectively, in
the presence of pyridine.

Fire-retardant phospholane solvents that are
useful in the invention include those having the
structure as shown in Formula (II),

15

(II)

$$\begin{bmatrix} O \\ O \end{bmatrix} P \begin{matrix} R^5 \\ OR^6 \end{matrix}$$

wherein R^5 and R^6 are as defined above. Commercially
20   available phospholanes include Antiblaze® 19 and
Antiblaze® 1045 (Albright and Wilson). Such phospholanes
can be synthesized by one of skill in the art using
conventional synthetic techniques (see, e.g., U.S. Patent
Nos. 3,789,091 and 3,849,368 to Anderson et al.). For
25   example, the phospholanes

30

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$$\begin{array}{c}\left[\begin{array}{c}-O \quad O \\ \diagdown P \diagup \\ -O \quad OC_2H_5\end{array}\right]\end{array}$$

$$\begin{array}{c}\left[\begin{array}{c}-O \quad O \\ \diagdown P \diagup \\ -O \quad OC_2H_4OCH_3\end{array}\right]\end{array}$$

5

$$\begin{array}{c}\left[\begin{array}{c}-O \quad O \\ \diagdown P \diagup \\ -O \quad OCH_2CF_3\end{array}\right]\end{array}$$

$$\begin{array}{c}\left[\begin{array}{c}-O \quad O \\ \diagdown P \diagup \\ -O \quad OC_2H_4OCOCH_3\end{array}\right]\end{array}$$

and

10

$$\begin{array}{c}\left[\begin{array}{c}-O \quad O \\ \diagdown P \diagup \\ -O \quad OC_2H_4OC_2H_4OCH_3\end{array}\right]\end{array}$$

15 can be synthesized from the correspondent 2-chloro-1,3,2-
    dioxaphospholane-2-oxide by reaction with ethanol, 2-
    methoxyethanol, 2,2,2-trifluoroethanol, 2-acetylethanol
    and 2-methoxyethoxyethanol, respectively. Alternative
    methods of preparing the phospholane

$$\begin{array}{c}\left[\begin{array}{c}-O \quad O \\ \diagdown P \diagup \\ -O \quad OC_2H_5\end{array}\right]\end{array}$$

20

    have been reported by Kluger et al. (1969) *J. Am. Chem.
    Soc.* $\underline{91}$:6066 and Taira et al. (1984) *J. Org. Chem.*
    $\underline{49}$:4531. The phospholane

25

$$\begin{array}{c}\left[\begin{array}{c}-O \\ \diagdown \\ P-OC_2H_5 \\ \diagup \\ -O\end{array}\right]\end{array}$$
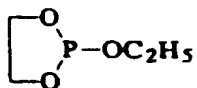
    can be prepared by reaction of 2-chloro-1,3,2-
30 dioxaphospholane with ethanol.
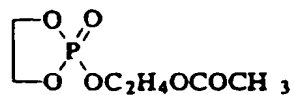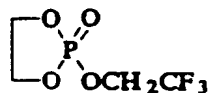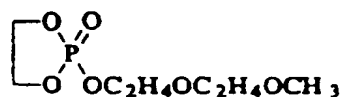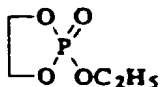
         Fire-retardant cyclophosphazene solvents that
    are useful in the invention include those having the
    structure as shown in Formula (III),

35

(III) $[N = P]_n$ with R^7 above and R^8 below

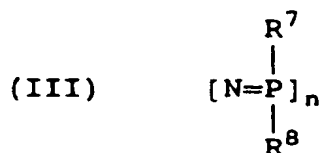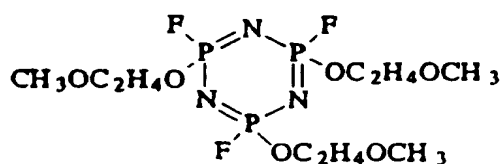wherein R^7, R^8 and n are defined as above. Such cyclophosphazenes can be prepared, for example, by reacting fluorophosphazenes with alkoxy alcohols. Thus, the cyclotriphosphazenes

$CH_3OC_2H_4O$ — cyclotriphosphazene ring with F, $OC_2H_4OCH_3$, F, $OC_2H_4OCH_3$ substituents

and

cyclotriphosphazene ring with F, F, $OC_2H_4OCH_3$, F, F substituents

can be prepared by reacting hexafluorotricyclophosphazene with 2-methoxyethanol under conditions adequate to achieve tri- and mono-substitution, respectively.

Fire-retardant silane solvents that are useful in the invention include those having the structure as shown in Formula (IV)

(IV) $R^{11} - \overset{\displaystyle R^{10}}{\underset{\displaystyle R^{13}}{Si}} - R^{12}$

wherein R^{10}, R^{11}, R^{12} and R^{13} are as defined above.

Among the preferred silane solvents are such
commercially available (e.g., Aldrich) silane compounds
as tetramethyl orthosilicate, tetraethyl orthosilicate,
tetrabutyl orthosilicate, and the like.

5   In addition, siloxane-based and phosphazene-
based solvents for electrolyte compositions can by
synthesized by functionalization of hydromethylsiloxanes
and cyclotriphosphazene with ether derivatives.
Hydrosiloxanes can be functionalized by reaction with

10   alcohols in the presence of a base, or by hydrosilylation
with allyl ethers.

Fire-retardant fluorinated carbonate solvents
that are useful in the invention include those having the
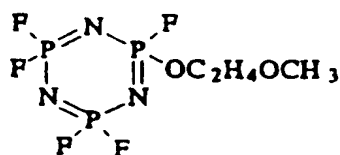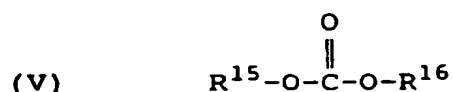structure as shown in Formula (V),

15

$$\text{(V)} \qquad R^{15}-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-R^{16}$$

wherein R^{15} and R^{16} are as defined above. Such

20   fluorinated carbonates can be synthesized by one of skill
in the art using conventional synthetic techniques as
described in, for example, U.S. Patent No. 3,455,954 to
Prager, European Patent Publication No. 0557167, Johnson
et al. (1973/74) *J. Fluorine Chem.* 3:1-6, Moore et al.

25   975) *J. Fluorine Chem.* 5:77-81, Walker et al. (1975) *J.
Fluorine Chem.* 5:135-139, and Hudlicky (1982) *J. Fluorine
Chem.* 20:649-658, the disclosures of which are
incorporated herein by reference.

Fire-retardant fluorinated polyether solvents

30   that are useful in the invention include those having the
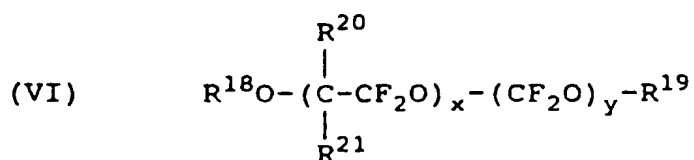structure shown in Formula (VI)

35

$$(VI) \qquad R^{18}O-\underset{\underset{R^{21}}{|}}{\overset{\overset{R^{20}}{|}}{C}}-CF_2O)_x-(CF_2O)_y-R^{19}$$

wherein R^{18}, R^{19}, R^{20} and R^{21} are as defined above. Fluorinated polyethers having Formula (VI) are commercially available as, for example, FOMBLIN® (Aldrich) or Galden® (PCR Inc., Gaineville, FL). Alternatively, such fluorinated polyethers can be prepared using the method described by Sianesi et al. (1994) in *Organofluorine Chemistry: Principle and Applications*, Banks et al., eds., Plenum Press, NY, 431-467 (and references cited therein). One of skill in the art can also prepare such fluorinated polyethers using well-known methods of fluorination of commercially available polyethers such as described in, for example, Persico et al. (1985) *J. Am. Chem. Soc.* 107:1197-1201, Gerhardt et al. (1981) *J. Chem. Soc., Perkin Trans.* 1:1321, Gerhardt et al. (1979) *J. Polym. Sci., Polym. Chem. Ed.* 18:157, Gerhardt et al. (1978) *J. Org. Chem.* 43:4505, and Gerhardt et al. (1977) *J. Chem. Soc., Chem. Commun.* 8:259.

Optionally, at least one of R^1, R^2 and R^3, or R^6, or R^9, or at least one of R^{10}, R^{11}, R^{12} and R^{13} is modified to contain on the terminal carbon a substituent group having the structure $-R^{22}-O-C(O)-O-R^{23}$, wherein R^{22} and R^{23} are independently C_1-C_6 alkyl or wherein R^{22} and R^{23} are linked together to form a C_1-C_6 alkylene bridge, thereby forming a homo- (e.g., phosphate-phosphate dimers) or heterodimeric (e.g., phosphate-silane dimers) solvent.

In one embodiment of the invention, a fire-retardant electrolyte composition is prepared by dissolving a lithium salt in a fire-retardant solvent.

-20-

Preferred lithium salts include compounds of the formula Li-A, wherein A is an anion which may be Cl, CF_3SO_3, ClO_4, BF_4, Br, I, SCN, AsF_6, $N(CF_3SO_2)_2$, PF_6, SbF_6, $O(CO)R^\ell$, wherein R^ℓ is H, alkyl, aryl, alkenyl, halo,

5   haloalkyl, or the like. Preferred salts include, for example, $LiPF_6$, $LiAsF_6$, $LiN(SO_2CF_3)_2$, and mixtures thereof. Solutions of lithium salts in fire-retardant solvents are prepared to achieve approximately 0.2 M to 2.0 M lithium, preferably 0.5 M to 1.5 M lithium.

10   The term "lithium salt" is also intended to include single-ion conducting polymer electrolytes as described in commonly assigned U.S. Patent No. 5,061,581 to Narang et al., as well as in U.S. Patent Application Serial No. 08/372,216, entitled "Single-Ion Conducting

15   Solid Polymer Electrolytes," inventors Narang et al., filed on January 13, 1995. The disclosures of both of the aforementioned documents are incorporated herein by reference. Thus, a flame-retardant electrolyte composition may be prepared by dissolving a single-ion

20   conducting polymer electrolyte in one of the solvents described above to achieve approximately 0.2 M to 2.0 M lithium, preferably 0.5 M to 1.5 M lithium.

Single-ion conducting polymer electrolytes that are specifically contemplated for use herein include

25   those having the structure as shown in Formula (VII)

(VII)

$$\left[\begin{array}{c} R^{25} \\ | \\ Si - O \\ | \\ R^{24} \end{array} \right]_n$$

30
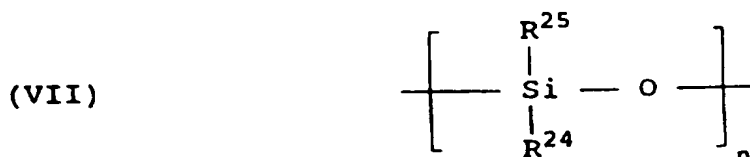
wherein:

R^{24} and R^{25} are individually selected from the group consisting of moieties having the structure

$-(CH_2)_{x1}(OCH_2CH_2)_{y1}(OCF_2CF_2)_{z1}SO_2R^{26}$

35

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-21-
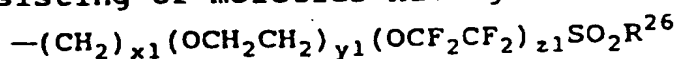
in which R^{26} is —OM, —N(M)SO$_2$CF$_3$, -N(M)C(O)CF$_3$ or —C(M)(SO$_2$CF$_3$)$_2$ and M is an alkali metal, preferably lithium, or wherein one of R^{24} and R^{25} has the structure

$$—(CH_2)_{x1}(OCH_2CH_2)_{y1}(OCF_2CF_2)_{z1}SO_2R^{26}$$
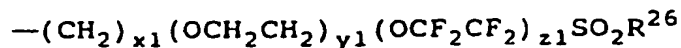
5   and the other is selected from the group consisting of hydrogen, lower alkyl, lower halo alkyl, lower alkenyl, fluorinated lower alkenyl, aryl and aralkylene;

x1 and z1 may be the same or different and are integers in the range of 1 to 100 inclusive;

10   y1 is an integer in the range of 0 to 100 inclusive; and

n is an integer indicating the number of mer units in the polymer.

Additional single-ion conducting polymer
15   electrolytes contemplated for use in the invention disclosed and claimed herein include co-polymers which contain first mer units having the structure as shown in Formula (VIII)

20   (VIII)

$$\left[\!\!\left[—(O)_{x2} — (CH_2)_{y2} — \underset{\underset{R^{28}}{|}}{\overset{\overset{R^{27}}{|}}{C}} — (CH_2)_{z2} \right]\!\!\right]$$
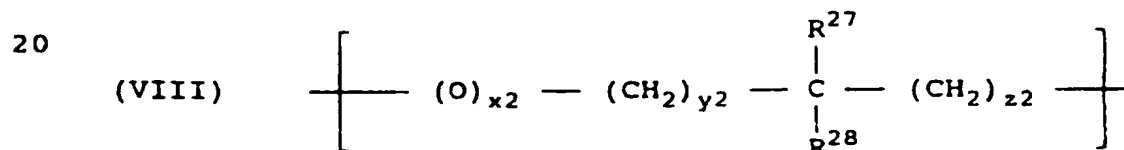
and second mer units having the structure as shown in
25   Formula (IX)

(IX)

$$\left[\!\!\left[—(O)_{x3} — (CH_2)_{y3} — \underset{\underset{R^{30}}{|}}{\overset{\overset{R^{29}}{|}}{C}} — (CH_2)_{z3} \right]\!\!\right]$$

30
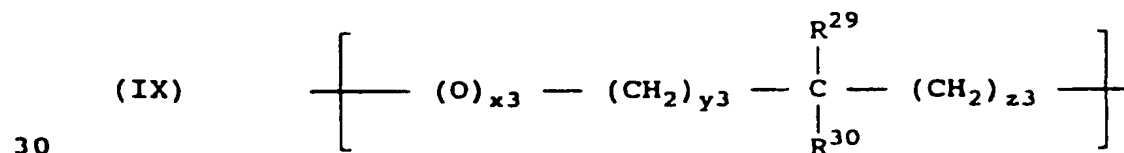
wherein:

R^{27} and R^{29} are independently selected from the group consisting of hydrogen, lower alkyl, lower alkoxy,
35   —COOR^{31} and —(CH$_2$)$_{n1}$—O—R^{31} in which R^{31} is lower alkyl or

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fluorinated lower alkyl and n1 is an integer in the range
of 1 to 6 inclusive;

R^{28} is $-(CH_2)_{x4}(OCH_2CH_2)_{y4}(OCF_2CF_2)_{z4}SO_2R^{26}$ in
which R^{26} is as defined above;

R^{30} is $-(CH_2)_{x5}(OCH_2CH_2)_{y5}OCH_3$ or $-COOR^{32}$ in
which R^{32} is lower alkyl or fluorinated lower alkyl; and

x2, x3, x4, x5, y2, y3, y4, y5, z2, z3 and z4
may be the same or different and are integers in the
range of 1 to 100 inclusive.

Accordingly, the fire-retardant electrolyte
composition may be formulated with a lithium salt of the
formula Li-A or a single-ion conducting polymer
electrolyte as described above.

In addition, a high dielectric constant solvent
such as ethylene carbonate, propylene carbonate, dimethyl
carbonate, diethoxyethane, diethyl carbonate,
dimethoxyethane, dipropyl carbonate, methoxyethoxy ethyl
ether, or mixtures thereof, may be added to the fire-
retardant electrolyte composition. Such formulations
have been shown to have conductivities at ambient
temperature higher than 1×10^{-3} S/cm.

The fire-retardant electrolyte compositions may
also be formulated with a CO_2-generating compound.
Incorporation of a CO_2-generating compound provides
enhanced battery cycling properties. For example, a
battery containing a CO_2-generating compound is capable
of being charged, discharged and recharged over a greater
number of such cycles. Such CO_2-generating additives may
be selected so that any decomposition by-products are
compatible both chemically and electrochemically with the
electrolyte and other battery materials. Examples of
such compounds include dicarbonates, esters, peresters,
dioxalates, acyl peroxides, peroxodicarbonates, Diels-
Alder adducts of carbon dioxide, and mixtures thereof.

One preferred CO_2 generator is di-*tert*-butyl dicarbonate ("DTBD").

Mechanically strong electrolyte films having conductivities higher than 10^{-3} S cm^{-1} may be formed from

5   a combination of: a solvent electrolyte as disclosed and claimed herein or mixtures of such solvent electrolytes; a film-forming polymeric material such as poly(vinylidene fluoride) ("PVdF"), polyacrylonitrile, copolymers of vinylidenefluoride and hexafluoropropylene, or the like,

10   preferably PVdF; a lithium salt of the formula Li-A, wherein A is as defined above, or a single-ion conducting polymer electrolyte as disclosed in Serial No. 08/372,216, incorporated by reference above; optionally, a high dielectric constant solvent such as propylene

15   carbonate ("PC"), ethylene carbonate ("EC"), dimethoxyethane ("DME"), and methoxyethoxy ethyl ether ("MEE"); and, optionally, a CO_2-generating compound. It may be necessary to add a glyme (e.g., dimethoxyethane ($C_4H_{10}O_2$), diglyme ($C_6H_{14}O_3$), triglyme ($C_8H_{18}O_4$),

20   tetraglyme ($C_{10}H_{22}O_5$) or so on) to form a homogeneous blend of the polymer electrolyte with PVdF; such compounds will typically serve not only as solvents but as additional plasticizing agents as well.

It will be appreciated that conductive

25   compositions formulated with the present electrolyte materials are also useful in the fabrication of fuel cells, sensors, supercapacitors, electrochromic devices, and the like, using manufacturing techniques well known to those skilled in the art, or readily available in the

30   relevant literature.

Manufacturing Methods:

A preferred method of manufacturing conductive compositions containing the novel electrolytes is a hot-

35   press technique for forming films. Such a method

-24-

typically involves: (a) forming a gel electrolyte
composition by combining (i) a lithium salt or single-ion
conducting polymer electrolyte (i.e., a polysiloxane of
Formula (I) or a copolymer containing mer units (II) and
5   (III)), with (ii) an effective amount of fire-retardant
solvent and (iii) an amount of PVdF or an alternative
material effective to enhance the mechanical strength of
the composition; (b) heating the resulting combination at
a temperature and for a time effective to form a fluid
10   solution; (c) pressing the fluid solution; (d) cooling
the solution; and (e) releasing the film so provided.
Alternative methods of manufacturing such conductive
compositions will be readily apparent to those skilled in
the art, or may be deduced from the relevant literature.
15

Industrial Applicability:
         Fire-retardant electrolyte compositions are
useful in a variety of contexts. An important utility is
in the fabrication of batteries. Batteries formulated
20   with the novel electrolyte compositions comprise a
positive electrode, or anode, a negative electrode, or
cathode, and electrolyte composition. Anodes and
cathodes may be fabricated from materials that are
commonly used in primary and/or secondary batteries. The
25   anode is typically lithium metal. Alternatively, a
carbon-based material such as petroleum coke or graphite,
intercalating metal oxides such as tungsten or iron
oxides, or other intercalating materials such as TiS_2,
may be used as the anode. The cathode is generally of a
30   lithium-containing material such as $LiCoO_2$, $LiMn_2O_4$ or
$LiNiO_2$; however, alternative materials could be used as
well, e.g., V_6O_{13}, MnO_2, FeS_2, or the like.
         It will be appreciated that conductive
compositions formulated with the novel electrolyte
35   compositions of the invention are also useful in the

fabrication of fuel cells, sensors, supercapacitors, electrochromic devices, and the like, using manufacturing techniques well known to those skilled in the art, or readily available in the relevant literature.

5

The following examples are intended to provide those of ordinary skill in the art with a complete
10 disclosure and description of how to make and use the novel electrolyte compositions of the invention, and are not intended to limit the scope of what the inventors regard as their invention in any way. Efforts have been made to ensure accuracy with respect to numbers used
15 (e.g., amounts, temperatures, etc), but some experimental error and deviation should, of course, be allowed for. Unless indicated otherwise, parts are parts by weight, temperatures are in degrees centigrade, and pressure is at or near atmospheric. All chemicals, reagents, and the
20 like, are commercially available or are otherwise readily synthesized using conventional techniques well known in the art.

Experimental
25 Equipment and Measurement Technique:
A. Physicochemical Characterization of Solvents and Electrolytes
        Dielectric Constant: The dielectric constant, ε, of fire-retardant solvents was determined in an
30 electrochemical cell containing two platinum electrodes. The electrodes had a diameter of 0.8 cm, area of 0.50 cm^2, and an interelectrode spacing of 0.1 cm, giving a sample volume of 0.05 cm^3. A Hewlett-Packard HP 4192A LF impedance analyzer was used to measure the capacitance C,
35 of the cell when filled with the candidate. ε was

calculated using $\varepsilon = C \backslash b_\varepsilon$, wherein b_ε is the cell constant. Two samples with known dielectric constants, water and trichloromethane, were used to calibrate the cell and calculate b_ε.

5   _Viscosity_: A Cannon-Ubbelohde viscometer was used to measure the viscosities of fire-retardant solvents. The kinematic viscosity, ν, was calculated using $\nu = b_\nu \tau$, wherein b_ν is the calibration constant of the viscometer and τ is time measured for a fixed volume
10   of solvent to flow through the capillary of the viscometer. Water and 1-propanol were used as standards to determine b_ν. The dynamic viscosity was calculated via $\eta = \nu \rho$ wherein ρ is the density of the sample.

          Electrical Conductivity: Conductivity cells
15   were fabricated from high-density polyethylene; two nickel plates were used as electrodes. The exposed area of the Ni plates was 0.2 cm^2; the interelectrode spacing was 1 cm. The conductivities of solutions prepared from fire-retardant solvents and lithium hexafluorophosphate
20   ($LiPF_6$) were measured using the AC impedance method. Typically, saturated solutions were prepared; generally, these were about 0.5 M. The conductivity, κ, is given by $\kappa = b_\kappa / R_\infty$ wherein b_κ is the cell constant and R_∞ is the real component of the AC impedance at high frequency (10
25   KHz). Cell constants were obtained by measuring the conductivities of aqueous KCl standard solutions of two concentrations. In cases wherein $\kappa > 5$ mS cm^{-1}, the conductivities of solutions prepared using other salts, e.g., lithium bis(trifluoromethanesulfonate)imide
30   ($LiN(CF_3SO_3)_2$), and the concentration dependence of the conductivities of $LiPF_6$ solutions were also measured.

          Conductivities were measured in 1 mol dm^{-3} $LiPF_6$ solutions, or in cases wherein $LiPF_6$ was poorly soluble in the solvent, saturated $LiPF_6$ solutions were
35   used.

B.   Electrochemical Characterization

Cyclic Voltammetry: Cyclic voltammograms of
the different electrodes were obtained in a three-
electrode cell under an argon atmosphere. The electrodes
5   were glassy carbon as working electrode, platinum as
counter electrode, and lithium as reference electrode.
In some cases, to test the stability of the solvent
against Li, Li was used as both working and counter
electrodes.

10   Cell Testing: Fire-retardant electrolytes that
had acceptable solvent properties determined as described
above were tested in a variety of electrochemical cells;

i.   Li|Ni cells. DC charge/discharge cycling
experiments were conducted in a high-density polyethylene
15   cell with a nickel working, lithium foil counter, and
lithium reference electrodes to determine the stability
of lithium metal in the solvent. Lithium was plated onto
the nickel electrode at a constant current density of 1
mA cm^{-2} for one hour; the total charge passed was 3.6 C
20   cm^{-2}. The cell was then cycled by alternately stripping
(discharge) and plating (charge) 1.2 C cm^{-2} of Li from
the nickel electrode at a constant current density of 1
mA cm^{-2} for twenty minutes or, during the stripping
process, until the nickel electrode potential reached
25   +1.0 V versus Li|Li$^+$. The cell was deemed to have failed
when the charge passed during the stripping step, Q_{strip},
was less than 50% of the charge passed during the plating
step, Q_{plate}. The parameters of interest are the number
of cycles before failure, N_{cy}, and the cycling
30   efficiency, Q_{eff}, which is calculated as Q_{eff} =
Q_{strip}/Q_{plate}. N_{cy} and Q_{eff} provide a measure of the
reactivity and an indication of the cyclability of the
solvent with Li.

ii.   Li|Li cells. Solvents were tested in
35   cells containing lithium anodes and cathodes and a

lithium reference electrode. A current density of 3 mA cm^{-2} and half-cycle times of 30 minutes were used to cycle the cell, although the effect of current density and charge/discharge time (i.e., depth of discharge) were

5   also parameters noted. An overpotential of 2.0 V at either Li electrode was considered as an indication of failure. The objective of these tests was to measure the lithium Figure of Merit ("FOM") in the solvent of interest and to judge therefrom the suitability of the

10   solvent for use in secondary cells.

        iii. Li Primary Cells. The high density polyethylene cells described above were used to test solvent electrolytes against cathodes used in commercial primary cells. The cathode materials used were iron

15   disulfide (FeS_2) and manganese dioxide (MnO_2). Cathodes were prepared by mixing 85 wt.% FeS_2 or MnO_2 and 5 wt.% carbon black with 10 wt.% PVdF binder then pressing the mixture onto nickel foil substrates (0.5 cm^2 to 2 cm^2). The cathodes were dried at 90°C overnight. Cells were

20   assembled from these cathodes, lithium foil anodes and a lithium reference electrode inside an argon-filled dry-box. The assembled cells were removed from the dry-box and discharged at various current densities using a Maccor battery tester. The objective of these tests was

25   to compare the electrochemical performance of the solvents with that of commercial primary cells. An Energizer® lithium cell (Li│FeS_2) (Eveready Battery Co.) was used as a baseline.

        iv.   Lithium Secondary Cells. The purpose of

30   these tests was to determine whether the nonflammable electrolytes could be used in lithium secondary, i.e., rechargeable, batteries. The experiments were performed using a cell with a lithium anode or a carbon anode, a $LiCoO_2$ or $LiMn_2O_4$ intercalation cathode, and a lithium

35   reference electrode. CO_2 or a CO_2 generator was used to

improve cyclability of the lithium. The cathodes and cells were prepared as described above. Cells were cycled galvanostatically at various current densities between cell voltage limits 4.2 V (charge) and 3.5 V

5   (discharge).

C.   Flammability Tests

        Two tests were used to determine the flammability of fire-retardant solvents. The first was

10   differential scanning calorimetry ("DSC") in which samples of the solvents were heated with and without lithium to expose potential thermal hazards associated with the solvent either by itself or in contact with materials likely to be present in a cell. The second

15   technique was accelerating rate calorimetry ("ARC"). The ARC is an adiabatic calorimeter in which heat evolved from the test sample is used to raise the sample temperature. ARC is conducted by placing a sample in a sample bomb inside an insulating jacket. In an ARC

20   analysis, the sample is heated to a preselected initial temperature and held a period of time to achieve thermal equilibrium. A search is then conducted to measure the rate of heat gain ("self-heating") of the sample. If the rate of self-heating is less than a preset rate after the

25   programmed time interval (typically $0.02°C \ min^{-1}$), the sample temperature is stepped to a new value, and the heat-wait-search sequence is repeated. Once a self-heating rate greater than the present value is measured, the heat-wait-search sequence is abandoned; the only

30   heating supplied to the calorimeter thereafter is that required to maintain the adiabatic condition between the sample and the jacket. Heat generated from the reaction inside the sample increases its temperature and pressure, thereby increasing the rate of the reaction. *See, e.g.,*

35   Townsend et al. (1980) *Thermochim. Acta* <u>37</u>:1. This

technique provide information for thermal hazard evaluation, material handling procedures, and can provide additional information on the energies of activation, storageability, and other fundamental thermokinetic

5   parameters that are not available using other techniques.

Example 1
Synthesis of

$$\left[\begin{array}{c} O \\ | \\ O \end{array}\right. \underset{P}{\overset{O}{\underset{\diagdown}{\parallel}}} \left.\begin{array}{c} \\ OC_2H_5 \end{array}\right]$$

10

Ethanol (2.3 gm) and pyridine (3.95 gm) were dissolved in 5 ml benzene and the solution was cooled to 0°C on an ice bath. 2-Chloro-1,3,2-dioxaphospholane-2-

15   oxide (5.985 gm) (Aldrich) in benzene (2 ml) was then added drop-wise to the solution to form a reaction mixture. The reaction mixture was then stirred at ambient temperature for 1 hour and heated at reflux for another hour.

20   The product was distilled and redistilled. The properties of the product corresponded to those previously reported (Kluger et al., *supra*; Taira et al., *supra*). The final distillate was used to prepare fire-retardant electrolyte compositions or fire-retardant gel

25   polymer electrolyte films employed in batteries.

Example 2
Synthesis of Tris-(methoxyethoxyethyl)phosphate
A solution containing 7.44 gm

30   2-methoxyethoxyethanol (Aldrich) and 7.7 gm of 4-di-methylaminopyridine ("DMAP") (Sigma) was prepared in 25 ml benzene and cooled to 0°C on an ice bath under an Ar atmosphere. Phosphorylchloride (3.06 gm) (Aldrich) in 5 ml benzene was added drop-wise to the solution which was

35   then stirred at ambient temperature for 3 hrs and

refluxed overnight. The reaction mixture was then
filtered, and chloroform (100 ml) was added and the
mixture was washed with brine (50 ml). The washed,
organic phase was dried over anhydrous Na_2SO_4 and rotary
5   evaporated to dryness, yielding 7.68 gm of product (a
96.6% yield). ^{1}H-NMR of the residue indicated that the
reaction had gone to completion. TLC chromatography in
ethyl acetate showed two spots, one of which corresponded
to DMAP and the other corresponded to the product.
10   The residue was chromatographed on silica gel
using ethyl acetate as the eluant. The product was
recovered in the second, third, and fourth 40-ml
fractions which were pooled. The pooled eluate was dried
under a vacuum to yield 4.5 gm (56% yield) of tris-
15   (methoxyethoxyethyl)phosphate which was used as is to
prepare fire-retardant electrolyte compositions or fire-
retardant gel polymer electrolyte films employed in
batteries.

20   Example 3
                          Synthesis of
            Tris-(2-methoxyethoxy)trifluorophosphazene
                  2-Methoxyethanol (2.28 gm) (Aldrich) was added
drop-wise to 20 ml of a suspension of 1.32 gm NaH (from a
25   60% w/v suspension in mineral oil) (Aldrich) in
tetrahydrofuran ("THF"), thereby forming the sodium salt.
The resultant solution was stirred at ambient temperature
for 1 hour and then added drop-wise to a solution of
hexafluorophosphazene (2.49 gm) (Aldrich) in 20 ml of dry
30   THF. The reaction mix was stirred at ambient temperature
overnight and then refluxed for six hours. The solvents
and other volatile materials were removed by rotary
evaporation. The residue was dissolved in chloroform and
filtered to removed salts. The chloroform was then
35   removed by rotary evaporation and the residue was passed

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through a flash chromatography column containing flash chromatography silica gel using ethyl acetate as the eluant. One fraction was collected and the product was isolated by removing the ethyl acetate by rotary

5   evaporation. The final product was used as is to prepare fire-retardant electrolyte compositions or fire-retardant gel polymer electrolyte films employed in batteries.

Example 4

10   Synthesis of
Tris-(ethoxycarbonyloxyethyl)phosphate
(2-Hydroxyethyl)ethylcarbonate
(HOC_2H_4-O-C(O)-O-CH_2CH_3) was prepared as follows. Chloroethylformate (10.8 gm; 0.1 mol) was added to a

15   mixture of ethylene glycol (31 gm; 0.5 mol) and pyridine (7.9 gm; 0.1 mol) in THF (80 ml) dropwise at 0°C under an inert atmosphere. The mixture thus formed was stirred overnight at ambient temperature. The THF was evaporated off and the residue was dissolved in methylene chloride

20   and washed several times with an aqueous saturated sodium chloride solution to remove ethylene glycol and salt. The organic layer was dried overnight over anhydrous Na_2SO_4. The solvent was distilled off, and the pure product was distilled at about 50°C under reduced

25   pressure.
           A solution containing 4.02 gm of (2-hydroxyethyl)ethylcarbonate and 7.7 gm of DMAP was prepared in 25 ml benzene and cooled to 0°C on an ice bath under an argon atmosphere. Phosphorylchloride (3.06

30   gm) in 5 ml benzene was added drop-wise to the solution which was then stirred at ambient temperature for 3 hrs and refluxed overnight. The reaction mixture was then filtered, chloroform (100 ml) was added and the mixture was washed with brine (50 ml). The washed, organic phase

35   was dried over anhydrous Na_2SO_4 and rotary evaporated to

dryness, yielding 7.68 gm of product (a 96.6% yield).
^{1}H-NMR of the residue indicated that the reaction had
gone to completion. TLC chromatography in ethyl acetate
showed two spots, one of which corresponded to the
product.

The residue was chromatographed on silica gel
as described in Example 2. The eluate was dried under a
vacuum to yield 3.9 gm (57% yield) of tris-
(ethoxycarbonyloxyethyl)phosphate which was used as is to
prepare fire-retardant electrolyte compositions or fire-
retardant gel polymer electrolyte films employed in
batteries.

<div align="center">

Example 5

Synthesis of

4-Dimethylethoxysilyl-1,2-butylene carbonate
</div>

A solution prepared from dimethylethoxysilane
(3 gm) (Aldrich), 1-ethenyl-ethylene carbonate (2.28 gm)
(Aldrich) and 200 mg Pt/C in 15 ml THF was refluxed for
18 hours under argon and cooled. Completion of the
reaction was confirmed by ^{1}H-NMR. After filtering the
reaction mixture, the solvent was removed by rotary
evaporation and the residual liquid was vacuum distilled.
Fractions were collected during the distillation process
(1: 35°C, 2 drops; 2: 90°C-100°C, 0.8 ml; 3: 125°C, 3
ml). The product (2.7 gm) was recovered in the third
fraction and used as is to prepare fire-retardant
electrolyte compositions or fire-retardant gel polymer
electrolyte films employed in batteries.

<u>Example 6</u>
<u>Preparation of a Lithium Battery</u>
<u>Containing Triethylphosphate</u>

This example describes the preparation of a
5   battery comprising a lithium metal anode, a $LiMn_2O_4$
cathode and a fire-retardant electrolyte.

The fire-retardant electrolyte was prepared to
have the following composition: $LiPF_6$ (1.0 M) (Aldrich)
in triethylphosphate ("TEP") (Aldrich) containing 10%
10   (v/v) dimethylpyrocarbonate (Aldrich) as a CO_2 generator.
The electrolyte solution was embedded in a 1 mil thick
separator (Celgard® 2500). The composite cathode was
prepared from 85 parts of $LiMn_2O_4$, 5 parts of acetylene
black and 10 parts PVdF dispersed in propylene
15   carbonate:ethylene carbonate (1:1 v/v). The composite
cathode paste formed upon heating to 170°C was then
applied on an aluminum current collector and hot pressed
(approximately 10,000 lbs of pressure for 1 min at 120°C-
130°C to form a film. After drying, the cathode was
20   back-filled with the liquid electrolyte. The anode, the
separator and the cathode were layered to form a battery
having a total thickness of about 15 mil.

FIG. 1 shows the potential profile for the
battery and each individual electrode upon cycling.
25

<u>Example 7</u>
<u>Full Cell Testing</u>
A.   Primary Batteries. Li|FeS₂ and Li|MnO₂
primary cells with lithium reference electrodes were
30   built to evaluate the performance of nonflammable
electrolytes. The cell body was made of polypropylene.
The solvents tested include triethylphosphate ("TEP"),
TEP dimer, methoxyethyl diethyl phosphate ("MTEP") and
mixtures thereof as indicated in Table 1.
35

Table 1

SUMMARY OF Li|FeS₂ AND Li|MnO₂ PRIMARY CELL TESTS

Cell Type	Electrolyte	Discharge Current Density (mA/cm²)	Cathode Capacity (mAh)	Anode Capacity (mAh)	Time (hr) EODV = 1.0V	Actual Capacity (mAh)	Energy Capacity (mWh)	Temp (°C)
Li|FeS₂	1 M LiPF₆ in TEP	0.24	~10	11.0	79.3	9.6	12.6	23
Li|FeS₂	1 M LiPF₆ in TEP	0.50	~9	11.0	35.5	8.9	11.4	23
Li|FeS₂	1 M LiPF₆ in TEP	1.50	~9	11.0	8.9	6.7	7.6	23
Li|FeS₂	1 M LiPF₆ in TEP	2.00	~9	11.0	2.9	2.9	3.0	23
Li|FeS₂	1 M LiPF₆ in TEP + DTBD (5%)	0.50	~9	11.0	35.9	9.0	12.0	23
Li|FeS₂	0.5 M LiPF₆ in TEP dimer	0.24	~10	11.0	100	12.0	16.0	23
Li|FeS₂	1 M LiPF₆ in MTEP	0.50	~10	11.0	42.0	10.5	13.5	23
Li|FeS₂	1 M LiPF₆ in TEP (47.5%) + MTEP (47.5%) + DTBD (5%)	0.50	~12	11.0	37.2	9.3	11.9	23
Li|FeS₂	1 M LiPF₆ in TEP (47.5%) + MTEP (47.5%) + DTBD (5%)	0.60	~12	11.0	24.2	7.3	8.0	23
Li|FeS₂	1 M LiPF₆ in TEP (47.5%) + MTEP (47.5%) + DTBD (5%)	0.60	~12	11.0	30.8	9.2	12.2	40
Li|FeS₂	1 M LiPF₆ in TEP (47.5%) + MTEP (47.5%) + DTBD (5%)	1.0	~12	11.0	7.3	3.6	3.3	23
Li|FeS₂	1 M LiPF₆ in TEP (47.5%) + MTEP (47.5%) + DTBD (5%)	1.0	~12	11.0	11.0	5.9	6.4	40
Li|MnO₂	1 M LiPF₆ in TEP	0.24	~6	11.0	47.0	5.0	15.3	23
Li|MnO₂	1 M LiPF₆ in TEP	0.50	~6	11.0	25.1	6.3	15.2	23
Li|MnO₂	1 M LiPF₆ in TEP (47.5%) + MTEP (47.5%) + DTBD (5%)	0.50	~6	11.0	17.6	4.4	10.0	23
Li|MnO₂	1 M LiPF₆ in TEP (47.5%) + MTEP (47.5%) + DTBD (5%)	0.50	~6	11.8	20.5	5.1	14.1	40
Li|MnO₂	1 M LiPF₆ in TEP (47.5%) + MTEP (47.5%) + DTBD (5%)	1.0	~6	11.8	8.3	4.1	11.0	40

In addition, the effect of added di-tert-butyl
dicarbonate ("DTBD") (Aldrich) was also investigated.
1 M $LiPF_6$ was the salt used in these tests. The
measurements were conducted at different discharge
5   current densities and temperatures.

The results from selected typical systems are
shown in Table 1. For the $Li|FeS_2$ system, the discharge
current densities applied range from 0.24 to 2.0 mA cm^{-2}.
Satisfactory results were obtained at current density of
10   1.0 mA cm^{-2} and lower. The cell voltages for most of the
$Li|FeS_2$ cells tested were quite stable and close to 1.5 V
during the entire discharging process until the
theoretical capacity of the Li anode was reached, as
indicated by a rapidly increasing anode potential. At
15   40°C, the cell shows better performance, presumably due
to higher conductivity and lower viscosity of the
electrolyte. Similar results were obtained for the
$Li|MnO_2$ system.

B.   Cyclability Tests ($Li|Li$ Cells). The
20   feasibility of using the fire-retardant electrolytes in a
lithium metal rechargeable battery was evaluated by
studying the cyclability of lithium between two lithium
electrodes. The DC cycling tests of $Li|Li$ cells with
lithium reference electrodes were conducted in TEP, TEP
25   dimer, MTEP, tri(methoxyethyl)phosphate ("TMEP"), and
mixtures thereof with salts including $LiPF_6$,
$LiN(CF_3SO_2)_2$, $LiCF_3SO_3$, and $LiAsF_6$. A current density of
3 mA cm^{-2} and half-cycle time of 30 min. were the
conditions used in these experiments. An overpotential
30   of 2.0 V or higher for either Li electrode was considered
an indication of failure. The results of these tests are
presented in Table 2.

35

Table 2
SUMMARY OF DC CYCLING TESTS FOR Li|Li CELLS

Solvent	Salt and Concentration	Current Density (mA/cm^2)	1/2 Cycle Time (min)	Number of Cycles	Temp. (°C)
TEP	1 M LiPF$_6$	1.0	20	160	23
TEP	1 M LiPF$_6$	3.0	30	15	23
TEP	1 M LiPF$_6$, 0.1 M LiCO$_3$	3.0	30	8	23
TEP	1 M LiAsF$_6$	3.0	30	13	23
TEP	1 M Li Triflate	3.0	30	6	23
TEP	1 M Li Imide	5.0	30	2	23
TEP dimer	0.5 M LiPF$_6$	1.0	20	2	23
MTEP	1 M LiPF$_6$	3.0	30	15	23
TMEP	0.5 M LiPF$_6$	1.0	20	100	23
TEP + 5% PC	1 M LiPF$_6$	3.0	30	9	23
TEP + 1% DTBD	1 M LiPF$_6$	3.0	30	8	23
TEP + 5% DTBD	1 M LiPF$_6$	3.0	30	48	23
TEP + 5% DTBD	1 M LiPF$_6$	3.0	30	50	40
TEP + 5% DTBD	1 M LiPF$_6$	3.0	30	51	60
TEP (66%) + TEP dimer (34%)	1 M LiPF$_6$	1.0	20	52	23
TEP (63%) + TEP dimer (32%) + DTBD (5%)	1 M LiPF$_6$	1.0	20	335	23
TEP (45%) + TMEP (50%) + DTBD (5%)	0.75 M LiPF$_6$	3.0	30	6	23
MTEP + 5% DTBD	1 M LiPF$_6$	3.0	30	19	23
TEP (47.5%) + MTEP (47.5%) + DTBD (5%)	1 M LiPF$_6$	3.0	30	14	23

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Under the test conditions, the cell made with
the electrolyte composition of 1 M LiPF$_6$ in TEP can cycle
15 times. This system is equivalent to one full cycle of
total Li electrode capacity. The addition of 5% DTBD
5   improved the cyclability to 48 cycles, or three cycles of
the lithium. This improvement may be attributed to the
in situ decomposition of the dicarbonate to produce
carbon dioxide, thereby passivating the lithium electrode
surfaces.
10

Example 8
Materials Safety: Accelerating Rate Calorimetry

In order to assess the potential explosive
hazard of the fire-retardant electrolyte compositions,
15   the thermal characteristics of the solvent mixture TEP
(47.5% v/v), MTEP (47.5% v/v) and DTBD (5% v/v) were
evaluated in an aerobic environment in an accelerating
rate calorimeter (ARC) as described above.

FIG. 2 depicts the self-heating rate as a
20   function of temperature for strips of lithium metal
immersed in the TEP:MTEP:DTBD mixture and for the
electrolyte used in a commercial primary lithium battery.
In both cases, the electrolyte contains 1 M salt (LiPF$_6$
for the flame-retardant electrolyte and LiCF$_3$SO$_3$ for the
25   commercial battery electrolyte) and a strip of lithium
metal (10 mg). The total weight of the solution was
about 2.1 gm for both mixtures.

The results depicted in Figure 2 show that both
electrolytes exhibit exothermic behavior beginning at
30   about 160°C. The flame-retardant electrolyte system
exhibits a maximum self-heating rate of 0.38°C min^{-1} at
178°C. By contrast, the commercial electrolyte exhibits
a larger exotherm with a maximum self-heating rate of
1.76°C min^{-1} at 191°C. The flame-retardant electrolyte
35   exhibits a second small exotherm between 200°C-230°C, but

the total heat liberated during these two exotherms is
less than that liberated during the single exotherm of
the commercial battery electrolyte.

5   Example 9
          Preparation of a Lithium Battery Containing
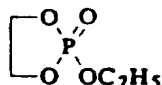   TEP and Ethylene Carbonate

          A solution of lithium bis(trifluoromethane-
sulfonate)imide (LiN(CF$_3$SO$_3$)$_2$) was prepared in a solvent
10   system composed of ethylene carbonate:TEP (1:1). The
room temperature conductivity of this solution was found
to be 2.82 x 10^{-3} S cm^{-1} by AC impendance analysis.

          A battery comprising a lithium metal anode, a
LiMn$_2$O$_4$ cathode and a fire-retardant electrolyte may be
15   made according to the procedure of Example 6 substituting
the ethylene carbonate:TEP solvent system for the TEP.
It is anticipated that the potential profile for the
battery and each individual electrode upon cycling will
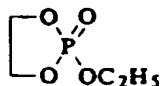be similar to that depicted in FIG. 1.

20

                         Example 10
          Preparation of a Lithium Battery Containing

$$\begin{bmatrix} O & O \\ & \diagdown \diagup \\ & P \\ O & OC_2H_5 \end{bmatrix}$$

25

          A battery comprising a lithium metal anode, a
LiMn$_2$O$_4$ cathode and a fire-retardant electrolyte may be
made according to the procedure of Example 9 substituting

$$\begin{bmatrix} O & O \\ & \diagdown \diagup \\ & P \\ O & OC_2H_5 \end{bmatrix}$$

30

prepared as described in Example 1 for the TEP in the
ethylene carbonate:TEP solvent system. It is anticipated
that the potential profile for the battery and each

35

individual electrode upon cycling will be similar to that
depicted in FIG. 1.

Example 11
Preparation of a Lithium Battery
Containing Tris-(methoxyethoxyethyl)phosphate

A battery comprising a lithium metal anode, a
$LiMn_2O_4$ cathode and a fire-retardant electrolyte may be
made according to the procedure of Example 9 substituting
tris-(methoxyethoxyethyl)phosphate prepared as described
in Example 2 for the TEP in the ethylene carbonate:TEP
solvent system. It is anticipated that the potential
profile for the battery and each individual electrode
upon cycling will be similar to that depicted in FIG. 1.

Example 12
Preparation of a Lithium Battery Containing
Tris-(2-Methoxyethoxy)trifluorophosphazene

A battery comprising a lithium metal anode, a
$LiMn_2O_4$ cathode and a fire-retardant electrolyte may be
made according to the procedure of Example 9 substituting
tris-(2-methoxyethoxy)trifluorophosphazene prepared as
described in Example 3 for the TEP in the ethylene
carbonate:TEP solvent system. It is anticipated that the
potential profile for the battery and each individual
electrode upon cycling will be similar to that depicted
in FIG. 1.

Example 13
Preparation of a Lithium Battery
Containing Tris-(ethoxycarbonyloxyethyl)phosphate

A battery comprising a lithium metal anode, a
$LiMn_2O_4$ cathode and a fire-retardant electrolyte may be
made according to the procedure of Example 9 substituting
tris-(ethoxycarbonyloxyethyl)phosphate prepared as

described in Example 4 for the TEP in the ethylene
carbonate:TEP solvent system. It is anticipated that the
potential profile for the battery and each individual
electrode upon cycling will be similar to that depicted
5   in FIG. 1.

Example 14
Preparation of a Lithium Battery Containing
1,1-Dimethyl-(1-ethylethylene carbonate)-ethoxysilane

10   A battery comprising a lithium metal anode, a
$LiMn_2O_4$ cathode and a fire-retardant electrolyte may be
made according to the procedure of Example 9 substituting
1,1-dimethyl-(1-ethylethylene carbonate)-ethoxysilane
prepared as described in Example 5 for the TEP in the
15 ethylene carbonate:TEP solvent system. It is anticipated
that the potential profile for the battery and each
individual electrode upon cycling will be similar to that
depicted in FIG. 1.

20   ## Example 15
Preparation of a Lithium Battery Containing
Perfluoropropylene Carbonate
            A battery comprising a lithium metal anode, a
$LiMn_2O_4$ cathode and a fire-retardant electrolyte may be
25 made according to the procedure of Example 9 substituting
perfluoropropylene carbonate that can be prepared from
propylene carbonate using the method described in
European Patent Publication No. 0557167 for the TEP in
the ethylene carbonate:TEP solvent system. It is
30 anticipated that the potential profile for the battery
and each individual electrode upon cycling will be
similar to that depicted in FIG. 1.

35

Example 16
Preparation of a Lithium Battery Containing
a Perfluoropolyether

A battery comprising a lithium metal anode, a
5   LiMn$_2$O$_4$ cathode and a fire-retardant electrolyte may be
made according to the procedure of Example 9 substituting
perfluoropolyether Galden® HT90 (formula weight = 460)
(Harris Speciality Chemicals, PCR Division) for the TEP
in the ethylene carbonate:TEP solvent system. It is
10 anticipated that the potential profile for the battery
and each individual electrode upon cycling will be
similar to that depicted in FIG. 1.

Example 17
15   Preparation of a Lithium Battery Having a
Carbon Anode and Containing a Nonflammable Electrolyte

This example describes the preparation of a
battery comprising a carbon anode, a LiMn$_2$O$_4$ cathode and
a fire-retardant electrolyte.
20   An electrolyte solution of 1.0 M LiPF$_6$ in
ethylene carbonate:TEP (1:4 v/v) is embedded in a 1 mil
thick separator (Celgard® 2500). The carbon anode is
prepared from a composite of 90 parts coke carbon (Ucar
Carbon) and 10 parts PVdF in propylene carbonate:ethylene
25 carbonate (1:1 v/v). The composite is compounded at
about 170°C for about 5 min and then hot pressed (10,000
psi, 120°C-130°C for 1 min) onto a copper current
collector. After drying, the anode is back-filled with
the electrolyte solution. The cathode is prepared from
30 82 parts LiMn$_2$O$_4$, 12 parts acetylene black and 6 parts
PVdF dispersed in propylene carbonate:ethylene carbonate
(1:1 v/v). The cathode mixture is compounded at 170°C
for about 5 min and then applied onto an aluminum current
collector by hot pressing as above. After drying, the
35 cathode is back-filled with the liquid electrolyte. The

anode, the separator and the cathode are layered to form
a battery having a total thickness of about 15 mil.

Example 18
Fabrication of a Fire-Retardant
Electrolyte Film Containing TEP

In a dry box, $LiPF_6$ (1 gm), PVdF (2 gm) and TEP
(6 gm) were mixed and heated to 120°C until a clear melt
was obtained. The hot melt was poured into a mold and
pressed. After cooling to ambient temperature, a free-
standing film was formed. The conductivity of the film
was determined by AC impedance. The ambient temperature
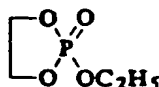conductivity was found to be 1.76×10^{-3} S cm^{-1}.

Example 19
Preparation of a Fire-Retardant Electrolyte
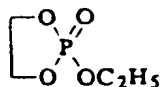### Film Containing TEP and Ethylene Carbonate

A conductive film comprising $LiPF_6$, PVdF and a
fire-retardant electrolyte may be made according to the
procedure of Example 18 substituting a solvent system
composed of ethylene carbonate:TEP (1:1) for the TEP. It
is anticipated that the AC impedance for the film will be
similar to that measured in Example 18.

Example 20
Fabrication of a Fire-Retardant
Electrolyte Film Containing

A conductive film comprising $LiPF_6$, PVdF and a
fire-retardant electrolyte may be made according to the
procedure of Example 19 substituting

$$\begin{bmatrix} O & O \\ & \diagdown \diagup \\ & P \\ O & OC_2H_5 \end{bmatrix}$$

prepared as described in Example 1 for the TEP in the
ethylene carbonate:TEP solvent system for the TEP. It is
anticipated that the AC impedance for the film will be
similar to that measured in Example 19.

                        Example 21
                Fabrication of a Fire-Retardant
                 Electrolyte Film Containing
           Tris-(methoxyethoxyethyl)phosphate
          A conductive film comprising $LiPF_6$, PVdF and a
fire-retardant electrolyte may be made according to the
procedure of Example 19 substituting tris-(methoxy-
ethoxyethyl)phosphate prepared as described in Example 2
for the TEP in the ethylene carbonate:TEP solvent system
for the TEP. It is anticipated that the AC impedance for
the film will be similar to that measured in Example 19.

                        Example 22
                Fabrication of a Fire-Retardant
                 Electrolyte Film Containing
          2-Methoxyethoxytrifluorophosphazene
          A conductive film comprising $LiPF_6$, PVdF and a
fire-retardant electrolyte may be made according to the
procedure of Example 19 substituting 2-methoxyethoxytri-
fluorophosphazene prepared as described in Example 3 for
the TEP in the ethylene carbonate:TEP solvent system for
the TEP. It is anticipated that the AC impedance for the
film will be similar to that measured in Example 19.

Example 23
Fabrication of a Fire-Retardant
Electrolyte Film Containing
Tris-(ethoxycarbonyloxyethyl)phosphate

5   A conductive film comprising $LiPF_6$, PVdF and a
fire-retardant electrolyte may be made according to the
procedure of Example 19 substituting tris-(ethoxy-
carbonyloxyethyl)phosphate prepared as described in
Example 4 for the TEP in the ethylene carbonate:TEP
10   solvent system for the TEP. It is anticipated that the
AC impedance for the film will be similar to that
measured in Example 19.

Example 24
Fabrication of a Fire-Retardant
Electrolyte Film Containing
1,1-Dimethyl-(1-ethylethylene carbonate)-ethoxysilane

          A conductive film comprising $LiPF_6$, PVdF and a
fire-retardant electrolyte may be made according to the
20   procedure of Example 19 substituting 1,1-dimethyl-(1-
ethylethylene carbonate)-ethoxysilane prepared as
described in Example 5 for the TEP in the ethylene
carbonate:TEP solvent system for the TEP. It is
anticipated that the AC impedance for the film will be
25   similar to that measured in Example 19.

Example 25
Fabrication of a Fire-Retardant
Electrolyte Film Containing
Perfluoropropylene Carbonate

          A conductive film comprising $LiPF_6$, PVdF and a
fire-retardant electrolyte may be made according to the
procedure of Example 19 substituting perfluoropropylene
carbonate that can be prepared from propylene carbonate
35   using the method described in European Patent Publication

No. 0557167 for the TEP in the ethylene carbonate:TEP
solvent system. It is anticipated that the AC impedance
for the film will be similar to that measured in Example
19.

5

Example 26
Fabrication of a Fire-Retardant
Electrolyte Film Containing
Perfluoropolyether

10   A conductive film comprising $LiPF_6$, PVdF and a
fire-retardant electrolyte may be made according to the
procedure of Example 19 substituting perfluoropolyether
Galden® HT90 (formula weight = 460) (Harris Speciality
Chemicals, PCR Division) for the TEP in the ethylene

15   carbonate:TEP solvent system. It is anticipated that the
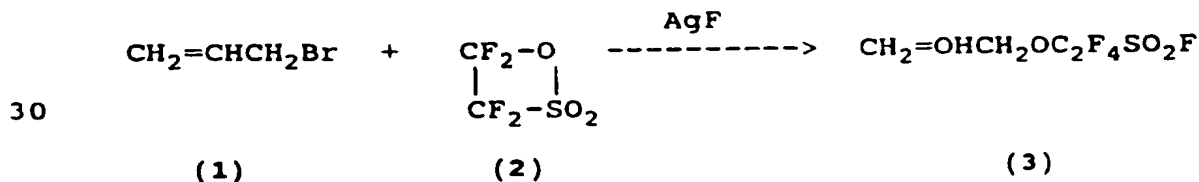AC impedance for the film will be similar to that
measured in Example 17.

Example 27
Fabrication of a Fire-Retardant
Electrolyte Film Containing a Polymethyl
Siloxane with $C_3H_6OC_2F_4SO_3Li$ Pendant Groups
          Lithium triflate polysiloxane (polymethyl
siloxane with $C_3H_6OC_2F_4SO_3Li$ pendant groups) was

25   synthesized as according to the following scheme and
procedures:

$$CH_2=CHCH_2Br \quad + \quad \overset{CF_2-O}{\underset{CF_2-SO_2}{|\quad\quad|}} \quad \xrightarrow{\quad AgF \quad} \quad CH_2=OHCH_2OC_2F_4SO_2F$$

30

    (1)   (2)   (3)

35

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$$(3) \ + \ \underset{(4)}{\overset{\overset{\displaystyle CH_3}{|}}{HSiCl_2}} \ \xrightarrow{\ \ CpA\ \ } \ \underset{(5)}{\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_3H_6OC_2F_4SO_2F}{|}}{Cl-Si-Cl}}}$$

$$(5) \ \xrightarrow[\text{ether}]{\ \ H_2O\ \ } \ \underset{(6)}{\left[\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_3H_6OC_2F_4SO_2F}{|}}{[SiO]_x}}\right]}$$

$$(6) \ + \ (CH_3)_3SiOSi(CH_3)_3 \ \longrightarrow \ \underset{(7)}{(CH_3)_3SiO-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_3H_6OC_2F_4SO_2F}{|}}{(SiO)_n}}-Si(CH_3)_3}$$

$$(7) \ + \ 2\ LiOH \ \xrightarrow[\text{THF/H}_2\text{O}]{} \ \underset{(8)}{CH_3)_3SiO-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_3H_6OC_2F_4SO_2F}{|}}{(SiO)_n}}-Si(CH_3)_3} \ + \ LiF$$
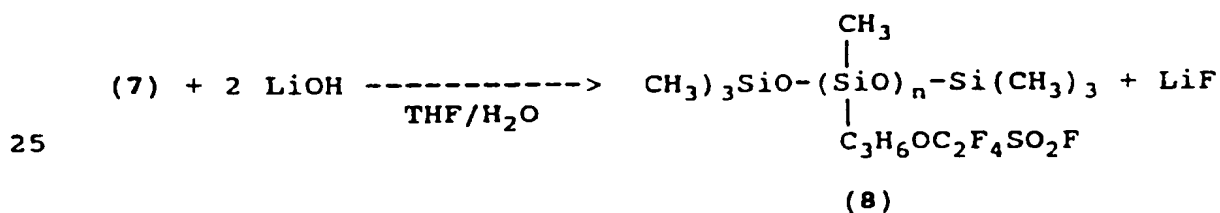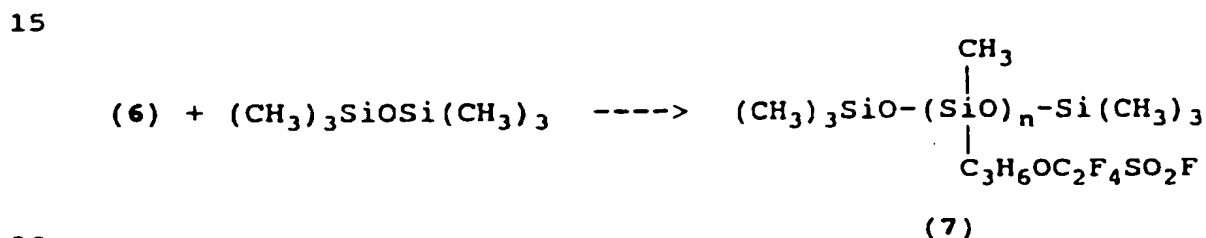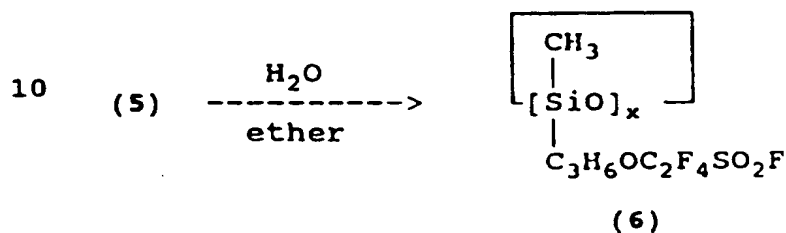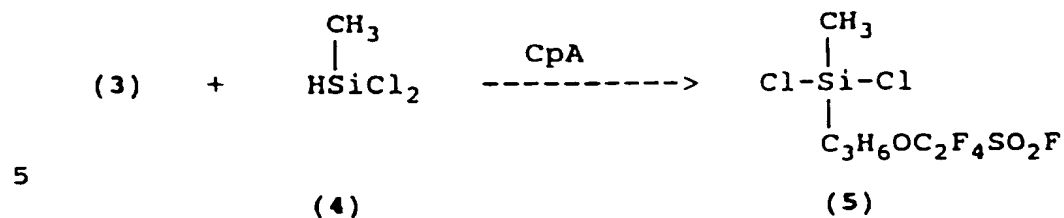
(a.) Preparation of Fluorosultone (2):

In a 500-ml Parr pressure reactor equipped with a magnetic stirrer, 50 ml of fresh sulfur trioxide was prepared by distillation of fuming sulfuric acid. Under stirring, tetrafluoroethylene was introduced continuously at the pressure of 30 psi. Exothermic reaction took place. The volume of the liquid content increased

gradually as the reaction proceeded. At the end of the
reaction, the crude product was purified by distillation.
A colorless liquid product was collected at the
temperature of 42-43°C. 162.9 g fluorosultone (2) was
5   obtained.

(b.) Preparation of (3):

In a 250-ml 3-neck flask equipped with a
magnetic stirrer and covered with aluminum foil, 63.44 g
(0.50 mol) of silver fluoride and 100 ml of anhydrous
10   diglyme were combined. The flask was cooled to -78°C and
90.04 g (0.50 mol) of fluorosultone (2) was added
dropwise. A clear solution was produced after 1 hr at
room temperature. The flask was again cooled to -78°C
and 60.49 g (0.50 mol) of allyl bromide (1) was added
15   dropwise. The reaction was heated at 45-50°C for 16
hours. The mixture was then filtered to remove AgBr.
The filtrate was poured into 100 ml water and the oily
layer which formed was washed three times with water and
dried over MgSo$_4$. Distillation gave 79.16 g (3), 76.1%,
20   bp 120-121°C. The identity of the product was confirmed
using ^{1}H NMR spectroscopy (^{1}H NMR (CDCl/δ): 4.60 (d, 2H,
CH$_2$=CHC$\underline{H}_2$O-); 5.34-5.47 (m, 2H, $\underline{CH}_2$=CH-); 5.89-5.98 (m,
1H, CH$_2$=$\underline{C}$HCH$_2$O-)).

(c.) Preparation of (5):

25   In a high pressure reactor, 72.69 g (0.35 mol)
of (3), 80.53 g (0.70 mol) dichloromethylsilane (4) and
0.46 g (1.1 mol) catalyst chloroplatinic acid were
combined. The reactor was sealed and filled with argon
to a pressure of 50 psi and then heated at 70-90°C for 22
30   hrs. After cooling to room temperature, the product was
then transferred under inert atmosphere to a flask using
a double-tip needle. Un-reacted dichloromethylsilane was
removed under reduced pressure. Distillation gave 85.89
g (5), 76%, bp 68-71°C/0.80 mm Hg. The identity of the
35   product was confirmed using ^{1}H NMR spectroscopy (^{1}H NMR

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(CDCl$_3$/δ): 0.82 (s, 3H, C̲H̲$_3$Si-); 1.15-1.25 (m, 2H, SiC̲H̲$_2$CH$_2$CH$_2$-); 1.9-2.0 (m, 2H, SiCH$_2$C̲H̲$_2$CH$_2$-); 4.1-4.2 (t, 2H, SiCH$_2$CH$_2$C̲H̲$_2$OC$_2$F$_4$SO$_2$F)).

(d.) Preparation of (6):

5   (5) (85.8 g, 0.27 mol) was taken up in anhydrous ether (50 mL), and the resultant solution was then added to a mixture of water (50 mL) and ether (50 mL) dropwise under stirring. At the end of the addition, the reaction was allowed to continue overnight. The oily

10   layer was separated from the aqueous layer. The aqueous layer was then extracted with ether (40 mL x 3), and the ether extract was combined with the oily layer product, washed with water until the water phase became neutral to pH paper, dried over anhydrous MgSO$_4$, filtered, and the

15   solvent was removed from the filtrate by rotary evaporator. The resulting colorless liquid residue was further dried at room temperature under 0.1 torr vacuum for 4 hours to yield 70.68 g. cyclosiloxane (6) (99%). The identity of the intermediate (6) was confirmed using

20   ^{1}H NMR spectroscopy (^{1}H NMR (CDCl$_3$/δ): 0.05-0.08 (m, 3H, C̲H̲$_3$Si-); 0.25-0.35 (m, 2H, SiC̲H̲$_2$CH$_2$CH$_2$-); 1.85-1.90 (broad, 2H, SiCH$_2$C̲H̲$_2$O-); 4.0-4.5 (broad, 2H, SiCH$_2$CH$_2$C̲H̲$_2$O)).

(e.) Preparation of (7):

25   The cyclosiloxane (6) (350 g, 1.305 mol)1 and hexamethyldisiloxane (42.4 g, 0.261 mol) were added to a round bottom flask with 10 drops of concentrated sulfuric acid and allowed to sit overnight. An additional 10 drops of concentrated sulfuric acid were then added and

30   the mixture was stirred for 24 hours. The mixture was then taken in methylene chloride and washed with water (2 x 500 mL) and then a saturated solution of NaCl containing a small amount of NaHCO$_3$. The solution was dried over MgSO$_4$ before removing the solvent by

35   evaporation.

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(f.)   Preparation of (8):

The sulfonyl fluoride polysiloxane (7) (59.80
g, 0.22 mol) was taken up in 270 mL THF. To the THF
solution, lithium hydroxide aqueous solution (10.67 g of
5   anhydrous LiOH, 0.44 mol, in 150 mL water) was added
dropwise in 6 hours. Theoretically, two moles of lithium
hydroxide are required to convert each sulfonyl fluoride
group to lithium sulfonate. However, lithium hydroxide
readily absorbs moisture because it is hygroscopic. A
10   slight excess of LiOH was added until the solution became
neutral using a pH meter as a monitor. The absence of
^{19}F NMR absorption at 123.5 ppm due to $-SO_2F$ confirmed
that all of the sulfonyl fluoride groups were converted
to lithium sulfonate. THF and water were then rotary
15   evaporated off. The residual white solid was dried at
50°C under 0.1 torr vacuum overnight.

The resulting crude product was dissolved in
200 mL acetone. The mixture was filtered in order to
remove LiF, and the filtrate was then concentrated. The
20   concentrated acetone solution was added dropwise to 600
mL of dry ether under stirring. The polymer product was
precipitated out. The polymer product (8) was then dried
at 70-80°C under 0.05 torr vacuum for 2 days, and the
pure product (8) was obtained in 93% yield. The identity
25   of the product (8) was confirmed using ^{1}H NMR
spectroscopy (^{1}H NMR (D_2O/δ): 0.21 (broad, 3H, CH_3Si-);
0.70 (broad, 2H, $SiCH_2CH_2CH_2-$); 1.80 (broad, 2H,
$SiCH_2\underline{CH_2}CH_2-$); 4.10 (broad, 2H, $SiCH_2CH_2\underline{CH_2}OC_2F_4SO_3Li$);
^{19}F NMR (D_2O/ppm): -5.61 (s, $-\underline{CF_2}CF_2SO_3Li$); -39.03 (s,
30     $-CF_2\underline{CF_2}SO_3Li$)).

(g.)   Preparation of the fire-retardant film:

Lithium triflate polysiloxane (1 gm), PVdF (2
gm) and a mixture of 1 part propylene carbonate, 1 part
ethylene carbonate and 2 parts triethylphosphate (6 gm)
35   were mixed and heated to 120°C until a clear melt was

obtained.   The melt was hot-pressed, then cooled to
ambient temperature to yield a clear, free-standing film.
The conductivity of this film was measured by AC
impedance.   The ambient temperature conductivity was
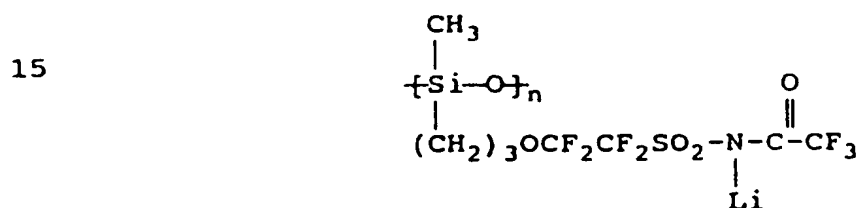5   found to be 7.85×10^{-4} S cm^{-1}.
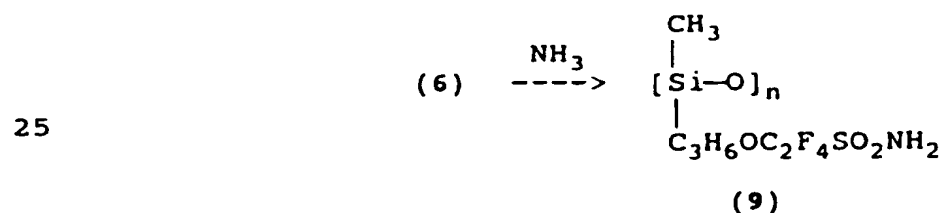

<u>Example 28</u>
<u>Fabrication of a Fire-Retardant</u>
<u>Electrolyte Film Containing a Polymethyl</u>
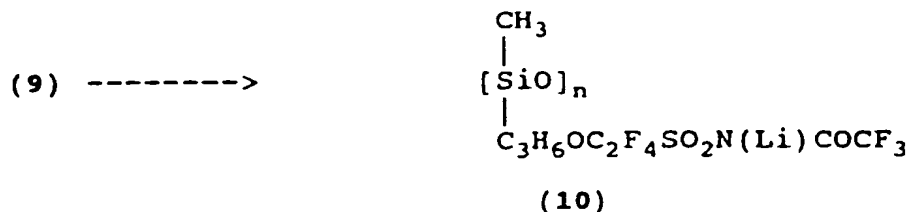10   <u>Siloxane with $C_3H_6OC_2F_4SO_2N(Li)C(O)CF_3$ Pendant Groups</u>
A lithium triflate polysiloxane single-ion
conducting polymer having the general structure

$$
\begin{array}{c}
CH_3 \\
| \\
+Si\!-\!O\!\!\}_n \qquad\qquad\qquad O \\
| \qquad\qquad\qquad\qquad\quad \| \\
(CH_2)_3OCF_2CF_2SO_2\!-\!N\!-\!C\!-\!CF_3 \\
| \\
Li
\end{array}
$$

15

20   was synthesized according to the following scheme and
procedures.

$$
(6) \xrightarrow{\ NH_3\ } \quad
\begin{array}{c}
CH_3 \\
| \\
[\,Si\!-\!O\,]_n \\
| \\
C_3H_6OC_2F_4SO_2NH_2
\end{array}
$$

25

(9)

30

35

$$
(9) \quad \text{-------->} \quad \begin{array}{c} CH_3 \\ | \\ [SiO]_n \\ | \\ C_3H_6OC_2F_4SO_2N(Li)COCF_3 \end{array}
$$

(10)

(a.) Preparation of (9):

The cyclosiloxane (6) prepared according to the procedure described in Example 27 (35.5 gm, 117 mmol) was dissolved in THF (40 mL) and added at -78°C under stirring to a mixture of ammonia (17.2 gm, 0.9 mol) in THF (220 mL). The mixture was stirred at -78°C for about one-half hour, then warmed to 0°C over about two hours. Stirring was continued at 0°C for about one hour. The mixture was allowed to warm to ambient temperature and then stirred overnight. The mixture was concentrated *in vacuo* and taken up in methanol (150 mL). Lithium hydroxide (9.9 gm, 236 mmol in 75 mL water) was added. The mixture was concentrated, then methanol (150 mL) was added, followed by 10 mL (120 mmol) of 12 N hydrochloric acid in 20 mL methanol. The product was purified by flash chromatography on silica gel (methylene choride:ethyl acetate 1:1).

(b.) Preparation of (10):

Sodium hydride (14.5 gm, 363 mmol, 60% in oil), washed with 3 x 60 ml of pentane, was added in eight portions to a mixture of (9) (38.5 gm, 129,6 mmol) in 550 mL of dimethoxyethane. The mixture was warmed to 50°C and stirring was continued for over 2.5 hours. The suspension thus formed was cooled to -70°C and trifluoroacetic anhydride (29.3 mL, 207.5 mmol) was added over 30 minutes. The slurry thus formed was stirred with a mechanical stirrer at about -25°C for 2.5 hours until all of the solid had dissolved. The mixture was allowed

to warm to room temperature and stirred overnight. The
crude product mixture was concentrated *in vacuo* and the
residue was taken up in 80 mL of CH_2Cl_2:ethyl acetate
(5:1) and purified by flash column chromatography on

5   silica gel (CH_2Cl_2:ethyl acetate 1:1) to yield the pure
sodium salt corresponding to (10). The latter was
converted to the lithium salt (10) by treatment on the
ion exchange resin IR120(+) previously treated with
water, then an aqueous solution of LiOH. The product

10   yield was greater than 80%.

(c.) Preparation of the fire-retardant film:

A conductive film can be made according to the
procedure of Example 27 substituting (10) for (8). It is
anticipated that the AC impedance for the film will be

15   similar to that measured in Example 27.

20

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35

We claim:

1.   A battery comprising an electrolyte which includes a compound which generates a

fire-retardant gas upon decomposition.

2.   The battery of claim 1 wherein the fire-retardant gas producing electrolyte

comprises a dicarbonate, ester, perester, dioxalate, acyl peroxide, peroxodicarbonates, or

Diels-Alder adducts of carbon dioxide, or mixtures thereof.

3.   The battery of claim 1 wherein the fire-retardant gas producing electrolyte

comprises di-*tert*-butyl dicarbonate.

4.   The battery of claim 1 wherein the gas comprises CO_2.

5.   The battery of claim 1 further characterized by at least one of the following:

        (A) the electrolyte includes a silane;

        (B) the electrolyte includes a phosphate;

        (C) the electrolyte includes a halogenated carbonate;

        (D) the electrolyte includes a cyclophosphazene;

        (E) the electrolyte includes a phospholane;

        (F) the electrolyte includes a fluorinated polyether.

6.   The battery of claim 5 wherein the fire-retardant gas producing electrolyte

comprises a dicarbonate, ester, perester, dioxalate, acyl peroxide, peroxodicarbonates, or

Diels-Alder adducts of carbon dioxide, or mixtures thereof.

7.   The battery of claim 5 wherein the fire-retardant gas producing electrolyte

comprises di-*tert*-butyl dicarbonate.

8.   The battery of claim 5 wherein the gas comprises CO_2.

9.   The battery of claim 5 wherein the silane comprises:
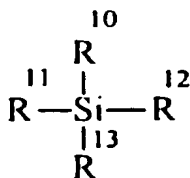
$$R^{11} - \underset{\underset{R^{13}}{|}}{\overset{\overset{R^{10}}{|}}{Si}} - R^{12}$$

wherein R^{10}, R^{11}, R^{12} and R^{13} are independently selected from the group consisting of (a) C_1-

C_6 alkyl terminally substituted with 0 to 3 halogen atoms and containing 0 to 3 ether

linkages and (b) -OR^{14} wherein R^{14} is C_1-C_6 alkyl terminally substituted with 0 to 3 halogen

atoms and containing 0 to 3 ether linkages, and optionally wherein two or more compounds

of structure (IV) are linked together by a siloxane linkage.

10.   The battery of claim 5 wherein the phosphate having the following structure:
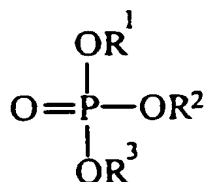
$$O = \underset{\underset{OR^3}{|}}{\overset{\overset{OR^1}{|}}{P}} - OR^2$$

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wherein R^1, R^2 and R^3 are independently selected from the group consisting of (a) C_1-C_6 alkyl terminally substituted with 0 to 3 halogen atoms and containing 0 to 3 ether linkages, (b) $Si(R^4)_3$ and (c) $B(OR^4)_{21}$ wherein the R^4s are independently C_1-C_6 alkyl containing 0 to 3 ether linkages or C_1-C_3 alkoxy, and optionally wherein two or more compounds of structure (I) are linked together by an ether linkage.

11. The battery of claim 5 wherein the halogenated carbonate has the following structure:
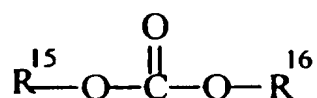
$$R^{15}-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-R^{16}$$

wherein R^{15} and R^{16} are independently selected from the group consisting of (a) perfluorinated or partially fluorinated C_1-C_{10} alkyl containing 0 to 3 ether linkages and (b) -OR^{17} wherein R^{17} is perfluorinated or partially fluorinated C_1-C_{10} alkyl containing 0 to 3 ether linkages or wherein R^{15} and R^{16} are linked together to form a perfluorinated or partially fluorinated C_1-C_{10} alkyl bridge, and wherein the halogenated carbonate may have multiple carbonate groups.

12. The battery of claim 5 wherein the cyclophosphazene has the following structure:
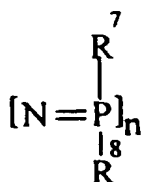
$$[N=\overset{\overset{\displaystyle R^7}{|}}{\underset{\underset{\displaystyle R^8}{|}}{P}}]_n$$

wherein n is an integer from 3 to 6 and R^7 and R^8 are independently selected from the group consisting of hydrogen, halogen and -OR^9 wherein R^9 is C_1-C_6 alkyl terminally substituted with 0 to 3 halogen atoms and containing 0 to 3 ether linkages, with the proviso that when one of R^7 or R^8 is -OR^9, the other is halogen.

13. The battery of claim 5 wherein the phospholane has the following structure:

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$$\begin{bmatrix} O \\ O \end{bmatrix} P \begin{matrix} R^5 \\ OR^6 \end{matrix}$$
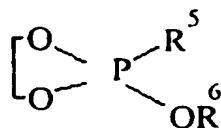
wherein R^5 is selected from the group consisting of oxy or a pair of electrons and, when R^5 is a pair of electrons, R^6 is $C_1.C_6$ alkyl terminally substituted with 0 to 3 halogen atoms and containing 0 to 3 ether linkages.

14.   The battery of claim 5 wherein the fluorinated polyether has the following structure:
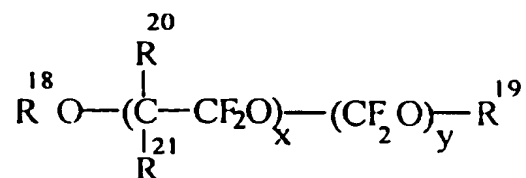
$$R^{18}O{-}(\underset{\underset{R^{21}}{|}}{\overset{\overset{R^{20}}{|}}{C}}{-}CF_2O)_x{-}(CF_2O)_y{-}R^{19}$$

wherein R^{18} and R^{19} are independently perfluorinated or partially flourinated C_1-C_{10} alkyl, R^{20} and R^{21} are independently selected from the group consisting of -F and perfluorinated or partially flourinated C_1-C_{10} alkyl, and x and y are independently selected with values ranging from 5 to 150.

15.   The battery of claim 5 wherein the fluorinated polyether has an average molecular weight between about 400 and 10,000.

INTERNATIONAL SEARCH REPORT

A.   CLASSIFICATION OF SUBJECT MATTER

IPC(6)   :H01M 6/16,18; 10/40

US CL   :429/192, 194

According to International Patent Classification (IPC) or to both national classification and IPC

B.   FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :   429/192, 194-197, 199, 30, 33; 252/62.2; 204/421

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C.   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 354,631 A (CHALONER-GILL et al) 11 October 1994	NONE
X	US 5,455,127 A (OLSEN et al) 03 October 1995, column 4, lines 10-24; column 6, lines 5-64; column 8, lines 38-41	1, 2, 5, 8
A,P	US 5,567,546 A (MALY-SCHREIBER et al) 22 October 1996	NONE
X,P	US 5,580,684 A (YOKOYAMA et al) 03 DECEMBER 1996 column 2, line 45- column 3, line 42; column 3, line 64- column 7, line 28; column 6, line 66-column 8, line 37.	1-5, 7-15

☐   Further documents are listed in the continuation of Box C.   ☐   See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 AUGUST 1997	1 4 SEP 1997

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	ANTHONY SKAPARS
Facsimile No. (703) 305-3230	Telephone No. 703-308-0661

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